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Selection Criteria and Methods for Testing Different Surface Materials for Contact Frying Processes

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Publication date:
2010

Document Version
Publisher's PDF, also known as Version of record

Citation (APA):
Ashokkumar, S. (2010). *Selection Criteria and Methods for Testing Different Surface Materials for Contact Frying Processes*. DTU Food.

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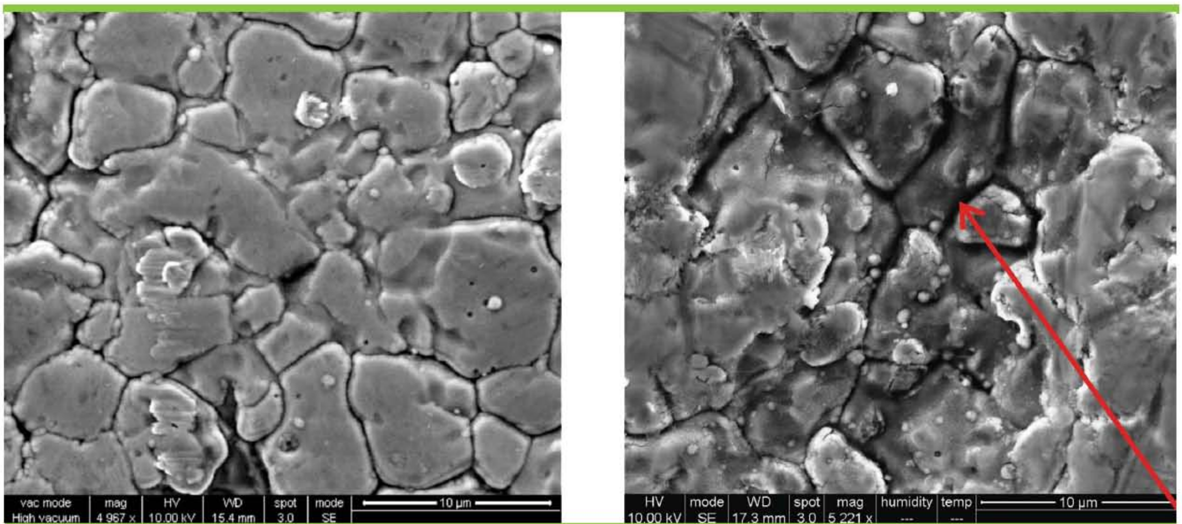

Residual surface contamination after frying on ZrO_2 and cleaning. Note the black carbon depostits in grain boundaries on disc after cleaning

Saranya Ashokkumar
PhD Thesis
2010

DTU Food
National Food Institute

PREFACE

The present thesis is the result of an industrial Ph.D.-project at Accoat A/S, Denmark under the supervision of Research Director, Jens Hinke and at Technical University of Denmark (National Food Institute, DTU FOOD) with supervision from Professor, dr.techn. Jens Adler-Nissen and Professor, Ph.D. Per Møller. The project was carried out in the period from August 15^{th} 2010 to December 15^{th} 2010.

The finanical support from the Danish Ministry of Science and Technology is gratefully acknowledged.

First of all, I would like to express my sincere gratitude to my principal supervisor Professor Jens Adler-Nissen for his guidance, advices and fruitful discussions throughout the project. I extend my warm thanks to Professor, Per Møller and Research Director, Jens Hinke for sharing their ideas and for the inspiring discussions. It has been a great experience working with you all in this project. Susie-Ann Spiegelhauer is sincerely acknowledged for providing helpful suggestions on the experiments at Accoat A/S. I will also thank Jette Høj for her great help to make last-time linguistic corrections for my thesis.

I would like to acknowledge my appreciation to all my colleagues at Accoat A/S, Denmark and at National Food Institute, Technical University of Denmark for being very helpful and making the work place lively and very happy. I express my thanks to my office mates for creating an inspiring and relaxed work atmosphere. The timely help from Gine Ørnholt Zammit in printing the thesis is gratefully acknowledged.

Finally, I wish to thank my friends Priyanka and Honey who have always given the helpful support whenever needed. A great appreciation to my mother Rukmani and my two brothers, Thiru and Shiva, who gave me confidence to carry out this project for more than three years at Denmark. A special gratitude to my fiance Azhaarudeen for his love, great support and constant encouragement for the whole duration of this project.

Lyngby, December 2010

Saranya Ashokkumar

SUMMARY

Inner surfaces of industrial process equipment for food are often coated to give the surfaces particular properties with respect to adhesion and cleanability. Existing coating materials (PTFE (Teflon®) or silicone based polymers) suffer from drawbacks when used in contact frying, because these coatings are not mechanically stable, they do not tolerate high enough temperatures (above 260^0 C) to give the right product quality, and the surfaces wear easily calling for regular service of the equipment. The present project concerns an investigation of the possibilities of replacing the widely used non-stick PTFE coating with new surface coating solutions for contact frying processes, where the food is fried by contact with a hot surface (pan frying, stir frying). The main objective of the present work is to develop suitable, scientifically based methods for selecting and testing different surface materials for contact frying processes.

The surfaces selected for this purpose cover a wide spectrum of materials that range from hydrophobic to hydrophilic materials. The different surface materials investigated include stainless steel (reference), aluminium (Al Mg 5754), PTFE (polytetrafluoroethylene), silicone, quasicrystalline alloys (Al, Fe, Cr) and ceramic coatings: zirconium oxide (ZrO_2), zirconium nitride (ZrN) and titanium aluminium nitride (TiAlN) with two different levels of smoothness. In order to investigate the non-stick and cleaning properties of different surfaces, an experimental rig has been constructed which enabled a controlled fouling of different coatings on steel and aluminium substrates under realistic frying conditions. A subjective rating procedure was employed for screening different surfaces according to their non-stick properties when used for frying of a model pancake. In order to validate the subjective assessment by means of an objective method, a technique has been developed to measure the force of adhesion between the pancake and the different surfaces; a good correlation was obtained between the subjective and the objective method up to a limiting force of adhesion. Above that the pancake disintegrated by cohesive failure. Differences in the non-stick properties of different ceramic surfaces could mostly be explained by differences in the surface topography. The interfacial contact between the pancake and the frying surface was lower for a rough surface than a smooth surface; thus, a rough surface resulted in significantly less sticking than a smooth (electro-polished) surface. The relevance of using an oven to demonstrate the non-stick and cleaning properties of different surfaces for contact frying processes was also examined, and our results demonstrated that it is not realistic to test non-stick properties for contact frying processes by using a convective oven, as seems to be an established practice in industry.

The different surfaces were analyzed for their cleaning properties by performing contact frying experiments with different foods, i.e. turkey meat, carrots and sweet potatoes at different temperatures with and without the use of oil; the different surfaces were cleaned by a combination of chemical and mechanical cleaning and the surfaces were subjectively rated for their cleanability. The results revealed that the cleanability of different surfaces was significantly reduced by the use of oil, especially at high temperatures.

The different surfaces were re-used after each frying experiment, and after completion of the whole set of experiments they were cleaned and analyzed in scanning electron microscopy (SEM) in order to inspect their cleanability. Energy dispersive spectroscopy (EDS) was employed to elucidate the difference in elemental composition between stained and unstained spots in different surfaces that were clearly visible using SEM. In most of the surfaces, surface defects, grooves and scratches retained more carbon-containing residues confirming the significance of mechanical interlocking phenomenon on cleanability issues.

Contact angle measurements were carried out with vegetable oil on different surfaces at different temperatures in order to study the relation between wettability and cleanability. The measured contact angle values gave useful information for grouping easy-clean polymer materials from the other materials; for the latter group, there is no direct relation between contact angle and cleanability, however. The study of different factors associated with wettability revealed that in addition to nature of the surface material, surface defects and surface roughness play a significant role.

The wear resistance of the coatings was tested by performing abrasive wear experiments. The ceramic coatings: TiAlN and ZrN were found to show the best wear resistance properties. The experiments also revealed the poor wear resistance of stainless steel, aluminium, PTFE, silicone, zirconium oxide and quasicrystalline surfaces.

The knowledge gained in this project and the methods developed to systematically test and evaluate surfaces for their non-stick and cleaning properties provide an improved basis for selecting and testing new surfaces for contact frying processes.

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SAMMENDRAG

Indvendige overflader af industrielt procesudstyr til fødevarer er ofte forsynet med en belægning for at give overfladerne særlige egenskaber med hensyn til vedhæftning og rengørlighed. Eksisterende belægningsmaterialer (PTFE (Teflon ®) eller silikonebaserede polymerer) har imidlertid nogle ulemper, når de anvendes til kontaktstegning, da disse belægninger ikke er mekanisk stabile, de tolererer ikke temperaturer, der altid er høje nok (over 260ºC) til at frembringe den rette produktkvalitet, og overfladerne slides nemt, hvilket kræver regelmæssig service af udstyret. Nærværende projekt omhandler en undersøgelse af mulighederne for erstatning af den udbredt anvendte PTFE belægning med nye løsninger på overfladebehandlinger til kontaktstegningsprocesser, hvor maden steges ved kontakt med en varm overflade (pandestegning, wokstegning). Hovedformålet med indeværende arbejde er at udvikle egnede, videnskabeligt baserede metoder til udvælgelse og afprøvning af forskellige overfladematerialer til brug ved kontaktstegningsprocesser.

Overfladerne, som blev valgt til dette formål, dækker et bredt spektrum af materialer, der spænder fra hydrofobe til hydrofile materialer. De forskellige undersøgte materialer omfatter rustfrit stål (reference), aluminium (Al Mg 5754), PTFE (polytetrafluorethylen), silikone, quasikrystallinske legeringer (Al, Fe, Cr) og keramiske belægninger: zirconium oxid (ZrO_2), zirconium nitrid (ZrN) og titan aluminium nitrid (TiAlN) med to forskellige grader af overfladeruhed. For at kunne undersøge de forskellige overfladers non-stick egenskaber såvel som rengørlighed blev der konstrueret en forsøgsopstilling, som gjorde det muligt at skabe en kontrolleret tilsmudsning af de forskellige belægninger på stål- og aluminiumsubstrater under realistiske stegningsbetingelser. Der blev anvendt en subjektiv bedømmelsesprocedure til screeningen af de forskellige overflader i henhold til deres non-stick egenskaber, når de anvendes til stegning af en model pandekage. For at kunne validere den subjektive vurdering ved hjælp af en objektiv metode, blev der udviklet en teknik til at måle vedhæftningskraften mellem pandekagen og de forskellige overflader; en god korrelation blev opnået mellem den subjektive og den objektive metode op til en begrænsende vedhæftningskraft. Ved mekanisk påvirkning over denne grænseværdi ødelagdes pandekagen ved et indre brud. Forskelle i de forskellige keramiske overfladers non-stick egenskaber kunne overvejende forklares med forskelle i overfladetopografien. Grænsefladekontakten mellem pandekagen og stegeoverfladen var lavere for en ru overflade end for en glat overflade, og dermed resulterede en ru overflade i en betydeligt mindre fastklæbende

overflade end en glat (elektro-poleret) overflade. Relevansen af at bruge en ovn til at påvise de forskellige overfladers non-stick- og rengøringsegenskaber ved kontaktstegningsprocesser blev også undersøgt, og vores resultater viste, at det ikke er realistisk at afprøve non-stick egenskaber ved kontaktstegningsprocesser ved hjælp af en konvektionsovn, hvilket ellers er en fast praksis i industrien.

De forskellige overflader blev analyseret for deres rengørlighed ved at udføre kontaktstegningseksperimenter med forskellige fødevarer, her kalkunkød, gulerødder og søde kartofler ved forskellige temperaturer med og uden brug af olie; de forskellige overflader blev rengjort med en kombination af kemisk og mekanisk rensning, og overfladerne blev subjektivt vurderet for deres rengørlighed. Resultaterne viste, at rengørligheden for de forskellige overflader blev kraftigt reduceret ved brug af olie, især ved høje temperaturer.

De forskellige overflader blev genbrugt efter hvert stegeforsøg, og efter afslutningen af hele serien af forsøg blev de rengjort og analyseret ved hjælp af scanning elektronmikroskopi (SEM) for at inspicere deres rengørlighed. Energy dispersive spectroscopy (EDS) blev anvendt til at belyse forskellen i koncentrationerne af forskellige grundstoffer mellem de forskellige overfladers plettede og uplettede steder, som var synlige i SEM. I de fleste af overfladerne blev kulstofholdige rester tilbageholdt i overfladefejl, riller og ridser, hvilket bekræftede at mekanisk sammenlåsning (mechanical interlocking) har stor betydning for rengørligheden.

Der blev foretaget målinger af kontaktvinkler af vegetabilsk olie på forskellige overflader ved forskellige temperaturer for at studere sammenhængen mellem befugtningsevne og rengørlighed. De målte kontaktvinkelværdier gav brugbare oplysninger til at gruppere og adskille de rengøringsvenlige polymermaterialer fra de andre materialer; for sidstnævnte gruppe var der imidlertid ingen direkte korrelation mellem kontaktvinkel og renseevne. Undersøgelsen af forskellige faktorer, der er forbundet med befugtningsevnen, viste, at foruden karakteren af overflademateriale spiller også overfladedefekter og overfladeruhed en væsentlig rolle.

Belægningernes slidstyrke blev testet ved at udføre slibeafprøvninger med måling af massetabet. De keramiske belægninger: TiAlN og ZrN viste sig at have de bedste slidstyrkeegenskaber. Eksperimenterne afslørede også dårlige slidstyrker for rustfrit stål, aluminium, PTFE, silikone, zirconiumoxid og quasikrystallinske overflader.

Den viden, man har opnået gennem dette projektforløb, samt de metoder der er blevet udviklet til systematisk at teste og evaluere overflader for deres non-stick evner og rengøringsevner, har givet et bedre grundlag for valg og afprøvning af nye overflader til kontaktstegningsprocesser.

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Paper I

Ashokkumar, S., & Adler-Nissen, J. (2010). Evaluating the non-stick properties of different surface materials for contact frying. Journal of Food Engineering. (submitted September 30, 2010).

Paper II

Ashokkumar, S., Møller, P., & Adler-Nissen, J. (2010). Factors affecting the wettability of different surface materials with vegetable oil at high temperatures and its relation to cleanability. Journal of Colloid and Interface Science. (to be submitted on December 17, 2010).

Paper III

Ashokkumar, S., Thomsen, B. R., Hinke, J., Møller, P., & Adler-Nissen, J. (2010). Cleanability evaluation of different surfaces by fouling from contact frying of foods. In *Proceedings of Fouling and Cleaning in Food Processing 2010* (pp. 24-33). 22-24 March2010, University of Cambridge, UK.

Paper IV

Feyissa, A. H., Gernaey, K. V., Ashokkumar, S., & Adler-Nissen, J. (2010). Modelling of coupled heat and mass transfer during a contact baking process. Journal of Food Engineering, (submitted November 1, 2010).

SYMBOLS AND ABBREVIATIONS

Symbols

PTFE	Polytetrafluoroethylene	
ΔG	Gibb's free energy	[kcal/mol]
ZrO_2	Zirconium oxide	
ZrN	Zirconium nitride	
TiAlN	Titanium aluminium nitride	
UP 316 SS	Unpolished stainless steel	
EP 316 SS	Electropolished stainless steel	
R_a	Roughness	[µm]
PVD	Physical Vapour Deposition	
SEM	Scanning Electron Microscopy	
EDS	Energy Dispersive Spectroscopy	

CHAPTER 1
INTRODUCTION

Contact frying is the frying of food by heat transferred through direct contact with a hot surface, usually of mild steel, stainless steel, cast iron or aluminium. Pan frying is a classical method of contact frying in household scale while in industrial scale contact frying is carried out on brat pans or on continuous frying bands.

During the frying process many heat induced reactions will take place among the major food components, such as Maillard reactions, caramelisation and polymerisation of unsaturated fatty acids (DeMan, 1999; Gogus et al. 2000; Therdthai and Zhou, 2003). The formation of these degradation compounds has both positive and negative aspects. The positive are that they are the main contributors to the attractive flavour of a properly made frying crust; the negative that they form burnt deposits on surfaces in contact with the food. The contact frying process carried out at high temperatures will induce fouling or creation of burnt deposits; however, the best sensory quality of some foods, for example pan fried pork can be attained only by frying at high temperatures, normally over 200^{o}C (Meinert et al. 2007).

Traditionally, aluminium and steel are used as food contact surfaces in food industries. The advantages of aluminium are its high thermal conductivity, light weight and low price (Kaushik and Bala, 2010); however, it does not possess adequate corrosion resistance properties (Lewan, 2003), cannot be cleaned with alkaline detergents and aluminium ions may leach into the food (Faulkner 2001).

Stainless steel is a widely used material for designing food process equipments in food industries (Benezech et al. 2010; Lewan, 2003; Saikhwan et al. 2006; Verran et al. 2008; Yoon and Lund, 1994). Stainless steel has several advantages when used as a food contact surface since it has good corrosion resistance (Verran et al. 2008), good hygienic properties (Boulané-Petermann, 1996) and also possesses inert surface chemistry due to the formation of chromium oxide layer when it comes into contact with the atmosphere. Yet, formation of burnt layers cannot be avoided when frying with stainless steel since components (proteins, fats or carbohydrates) in the burned layer could react with the metal surface itself (Barham, 2001).

Adhesion of food components to stainless steel surface can be reduced by modifying the stainless steel surface; modification can generally be accomplished by coating the stainless steel surface with thin layer of a surface material such as PTFE, silicone, diamond like carbon (DLC), ceramics, etc. (Mauermann et al. 2009; Rosmaninho et al. 2007; Saikhwan et al. 2006).

Teflon® (PTFE) is a widely used non-stick coating due to its inert surface chemistry which is a consequence of the high bonding energy of the C-F bond (Balasubramanian and Puri, 2009; Zhang et al. 2009). However, PTFE coating and other organic polymers are not ideal for use in industrial food process equipments (Verran et al. 2000) since these coatings have poor heat conductivity, do not tolerate continuous exposure to high temperatures enough to give the right product quality, and the surfaces wear easily calling for regular service of the equipment. This is illustrated by the fact that food process equipment coated with PTFE is frequently brought to producers of PTFE coatings, for example Accoat A/S, Denmark in order to service the equipment by renewing its worn surface with a new PTFE coating. According to Accoat's experience, industrial baking trays and big frying plates are the most regular ones[1]. Thus, frying in the food industry is today based on equipment and processes that in many ways are not satisfactory in terms of long-term durability and maintenance costs. There is therefore a distinct need for new surface material solutions in order to achieve better durability, decrease down-time for cleaning and reduce maintenance costs. In these years surface coating technologies are developing rapidly, and it is conceivable that new resilient, low-friction coating materials are becoming within reach for use in food process equipment.

Accoat A/S is a coating manufacturing company at Denmark; they coat polymers (PTFE, polyurethane, silicone) on industrial equipments for different purposes. It is of great interest for a company like Accoat A/S to scientifically understand and master the phenomenon of non-stick and cleaning properties of different surface materials; thus, the industrial PhD project was initiated.

[1] In case of baking trays, the PTFE coated surface is worn within 4-6 months since the coating cannot resist the brush cleaning procedure performed for cleaning the trays. Moreover, severe wear occurred in spots where the surface was in contact with the bread during baking; in case of frying plates, maximum lifetime of the PTFE coating is one year if no metal utensils were in contact with the coated surface during the course of frying.

1.2. Food contact surfaces and their desired properties

The surface coating materials for food process equipment should possess many desired properties such as being easy to clean, smooth, inert, non-toxic, corrosion resistant, wear resistant, good hygiene, durability and low cost (Lewan, 2003; Verran et al. 2000; Stevens and Holah, 1993). The selection and testing of surfaces in this project were mainly focused on properties like non-stick, easy to clean, smooth, inert and wear resistance. In order to find widespread use of the selected surface in industrial environments, it is mandatory to satisfy these primary properties. Although cost is an important factor in this case, the cost criterion is not considered in this project.

Elucidation of the fouling and non-stick properties of surfaces used in contact frying processes is barely touched in the literature; relevant information is mainly found in patents where new surface modification techniques for cookware are described (Faulkner, 2001; Groll, 2006; Hayakawa, 2007). In such patents, practice-oriented methods were followed in which household frying pans are surface-modified according to the inventions described, and the pans are used to cook or fry different model food products in a standard procedure using a commercial household stove. For initial screening purposes it would, however, be advantageous if smaller samples coated with different surface materials can be used for preliminary testing of non-stick properties since modification of the whole frying pan is an expensive process. Furthermore, a frying platform with a definite control over surface temperature and heat flux is required in order to test different surface materials since an adequate control is not possible by frying on a household pan using a household stove; fouling using this procedure is also difficult to replicate from laboratory to laboratory. It was therefore decided that that the construction and validation of such an experimental platform was an important part of the present project.

The fouling and cleaning of open surfaces observed in frying and baking processes are less studied than fouling and cleaning in closed systems, perhaps because the open surfaces are usually accessible to manual cleaning with mechanical force (Holah, 2000; Salo, 2006). In the case of *closed* systems, numerous studies have been carried out to evaluate different surface materials for heat exchanger surfaces in order to reduce the problems of fouling and make cleaning more efficient (Muller-Steinhagen and Zhao, 1997; Rosmaninho et al. 1997; Yoon and Lund, 1994). However, experimental deposition of fouling layers at temperatures below or around 100^{o}C (Liu et al. 2006; Saikhwan et al. 2006; Rosmaninho et al., 2007; Mauermann et al. 2009) cannot suppose to result in a fouling layer which is analogous in composition and adhesive properties to that obtained by contact frying of meat, vegetables or batters, normally at 150-250^{o}C. In the search for enhanced surface solutions for contact frying the depositing of the fouling layer for testing the surface material should be made under reproducible conditions which are characteristic of typical frying processes. This needs an experimental frying platform as discussed above.

Food deposits remaining on the frying surface after frying may present problems with regard to sticking as well as cleaning. Stickiness is defined as "the force of adhesion when two surfaces are contacted with each other" (Hoseney and Smewing, 1999). Stickiness between foods and equipment surfaces is a complex phenomenon to measure (Hoseney and Smewing, 1999; Kilcast and Roberts, 1998; Liu et al. 2006). The sticking phenomenon is manifested by strong adhesive and cohesive forces between the reactive food components and the surface in contact (Balasubramanian and Puri, 2010). Although occasionally the food deposits do not stick to the frying surface, there is a gradual build up of deposits on the surface which need to be cleaned later on. In cases of food equipment sticking is not desired, particularly in bakery and confectionary industries (Dobraszczyk, 1996) while cleaning properties are critical in the processing of nearly all types of food.

In addition to that the surface coating materials should have good easy-release and easy-clean properties, they should also possess surface characteristics suitable for frying with oil. Faulkner (2001) states that "In terms of surface chemistry, a perfect non-stick cookware is one which would be wetted very well by olive oil but it should behave as hydrophobic as possible towards water-based dispersions". On surfaces like PTFE however, the oil form discrete droplets at the interface between food and surface which is not desirable for a good frying process (Faulkner, 2001). Wetting and surface tension measurements with water on a surface at room temperature have widely been used as an indication of easy-to-clean properties (see later in chapter 7). However, it seems more appropriate in the present project to study the wetting properties of different surfaces with oil at high temperatures. The reason for this is that at high temperatures water eventually evaporates but the oil used for frying cannot evaporate and remain on the frying surfaces hindering their cleanability.

Surface roughness is often considered to be an important factor influencing the cleanability of a surface (Boulané-Petermann, 1996; Whitehead and Verran, 2006; Wirtanen, 1995). In food industries, it is recommended that the roughness (R_a) of a food contact surface should not be more than 0.8 µm (Hilbert et al. 2003; Lewan, 2003). Stylus-based profilometers are usually employed to measure the roughness of a surface (Mattox, 1998). In addition to surface roughness, the size and type of surface irregularity has a determining effect on the cleanability of a surface (Hilbert, 2003; Leclercq-Perlat and Lalande, 1994). Furthermore, surfaces used in the food industries should be free from crevices, pits and folds (Lewan, 2003). Scanning electron microscope (SEM) is a commonly employed technique for examining the surface morphology; moreover, it is widely used for visually inspecting the cleanability of surfaces which are subjected to fouling and cleaning tests (Benezech et al. 2010; Holah and Thorpe, 1990; Whitehead et al. 2010). Surface materials selected for frying purposes should therefore be characterized for those surface topological properties which are believed to be relevant for sticking and fouling problems.

In general, all kinds of materials will usually be subjected to some degree of wear based on their usage and the functional environment (Verran, 2000). The materials used in the food industry should be able to resist wear; otherwise, their non-stick properties deteriorate rapidly during use. The durability of the surface materials could be assessed by analyzing their wear properties.

The main objective of the present work is to develop suitable, scientifically based methods for selecting and testing different surface materials for contact frying processes rather than to manufacture them. This is because at Accoat A/S, spray coating (see Chapter 3) is the main technique employed to coat the equipments; techniques other than spray coating are not readily available at Accoat A/S. The project is a multi-disciplinary task and therefore involved drawing upon the expertise from different fields such as surface engineering and food technology.

1.3 Outline of thesis

The thesis consists of eight chapters as follows:

I Introduction

The introduction starts with a description of contact frying process and existing problems with the surfaces which are traditionally used for contact frying processes. An overview of the studies concerning food adhesion and fouling issues in food industry is given. The properties that are desired for food contact surfaces and methods for finding the same are summarized.

II State of the art in coatings for contact frying surfaces

This chapter pertains to make a literature review on inventions relating to different surface modification techniques for contact frying surfaces and explains the basis for selection of particular surface materials for our study. The various test methods employed in the literature for evaluating different surface properties such as non-stick, cleaning, mechanical, etc. are also discussed in the chapter.

III Manufacture of coatings and their characterization techniques

This chapter describes about different techniques that are employed for producing the coatings by different suppliers. This chapter also explains the different methods employed to characterize different surfaces in order to understand their surface related properties.

IV Working principles and validation of the frying rig

Chapter IV deals with the working principles and validation of the frying rig that has been constructed primarily for investigating different surface materials under reproducible fouling conditions. The different experiments performed to validate the frying rig as well as the results summarized in this chapter are mainly based on the contents in Paper I.

V Methods for evaluating the non-stick properties of different surfaces

The chapter starts with an explanation of the adhesion phenomena and a discussion about different theories that are proposed for adhesion. This chapter also includes description of various methods that are employed to study the non-stick properties of different surfaces and a discussion of the results obtained using these methods.

VI Cleaning properties of different surfaces

The chapter begins with an introduction to fouling and a short review on scientific literature dealing with fouling and cleaning in food industries. An outline of different cleaning methods used in food industries is given. The different factors influencing the cleanability of different surfaces after frying different food models have been discussed in detail based on the results published in Paper III.

VII Cleanability examination of different surfaces using scanning electron microscopy and contact angle measurements

A short introduction about the usage of scanning electron microscopy (SEM) in examining surface cleanability is given followed by discussion of the results obtained during the analysis of cleaned frying surfaces using SEM. An introduction to the usage of contact angle measurements in cleanability studies is given. The results and discussion in this section is mostly based on the contents in Paper II.

VIII Conclusion and future perspectives

This chapter deals with conclusions obtained using this project and includes suggestions for future studies. The scientific understanding of the issues related to adhesion and fouling and the methods developed to systematically test and evaluate surfaces for their non-stick and cleaning properties provide an improved basis for selecting and testing new surfaces for contact frying processes.

CHAPTER 2

STATE OF THE ART IN COATINGS FOR CONTACT FRYING SURFACES

When the project was initially started, a literature survey was carried out to find scientific studies concerning new surface solutions for open food process equipments. It was soon realised that references in scientific journals were sparse; however, it was possible to find many patents describing household cookware with modified surfaces, and much of the practical approaches in the present project is inspired by these sources.

Among the different materials used for coating, the well-known material PTFE has been widely used as a non-stick coating for cookware since the 1960’s (Cahne, 1961). Silicone coatings have also been used for coating cookware even earlier (Webb and Koster, 1949). However, many drawbacks are encountered when a polymer (PTFE or silicone) is used as a coating material for the process equipments in the food industry (Muller-Steinhagen, 1997). The further inventions that followed PTFE were mainly focused on surface modification techniques in order to enhance the scratch and abrasion resistance of PTFE coated surfaces (Zigomalas, 1971; Welhouse, 1994; Cheng, 2004; Dorfschmidt ,1999; Felix et al. 2000; Hupf et al. 2000).

Zigomalas (1971) described a method where a substrate possessing annular protrusions was coated with PTFE. Welhouse’s (1994) invention consisted of a series of wave-like grooves embossed on the substrate of the cookware which was then coated with PTFE. The cookware coated in this manner are intended to have better abrasion resistance than the conventional PTFE coated cookware, because the coating material can be removed only in projected areas where the metal utensils make contact with the cookware, while the non-stick material remaining inside the grooves are still protected. Even though this type of cookware can resist abrasion to some extent the use of metal utensils slowly wear off the PTFE material from the grooves; in these cases, a long durability of the cookware cannot be expected.

Cheng (2004) described a method in which the inner surface of an aluminium cookware was subjected to a hard-anodising process in order to provide a hard and abrasion resistant surface for further application of PTFE coating; the outer surface of the cookware was coated with a layer of enamel. Dorfschmidt (1999) described a technique in which the substrate of the aluminium cookware was coated with a durable layer made of lacquer before subjecting the substrate to an anodising process; subsequently, the anodized surface was coated with PTFE. Felix et al. (2000)

developed a similar type of method in which a metal layer (aluminium or stainless steel) was thermally sprayed onto the substrate of the cookware after which a non-stick PTFE coating was sprayed onto the metal layer; in order to test the durability, the cookware was subjected to an accelerated in-home abuse test where it was used in a commercial kitchen for a period of four weeks; the authors reported that the cookware surface was free from any damage when visually inspected in the final step. Hupf et al. (2000) developed a method in which the substrate (stainless steel or aluminium) was mechanically roughened in order to provide better adhesion for an abrasion resistant layer (titanium or titanium nitride or titanium oxide) which was thermally sprayed onto the substrate; thereafter, a non-stick PTFE coating was sprayed onto the abrasion resistant layer. Using these methods, a good adhesion could be achieved between the PTFE coating and the substrate of the cookware as well as the mechanical properties of the PTFE coated cookware could be improved. Hence in our studies, anodized aluminium was chosen as the substrate for the non-stick silicone coating in order to test if the scratch and abrasion resistance properties of silicone could be improved by coating it on an anodized layer which is hard and resistant to wear.

Ge and Mo (2005) pointed out that the non-stick coating deposited by the above mentioned procedures can penetrate through the non-continuous thermally sprayed layers where a direct deposition of the non-stick coating on the cookware substrate could be possible, which may result in galvanic corrosion between the substrate and the abrasion resistant layer. In order to overcome this problem, the process was modified by Ge and Mo (2005); the cookware substrate was roughened followed by the deposition of a continuous ceramic coating (titanium aluminium nitride or titanium aluminium chromium nitride) by a physical vapour deposition process, onto which a non-stick coating (PTFE resin) was applied. The cookware invented by this method was subjected to blistering tests with a salty-based solution (salt water with a pH of 8.0) and an acidic-based solution (tomato sauce with a pH of 4.5) for 16 hours. The pans were then washed with hot water and detergent using a soft brush in order to remove any adhering deposits, and in the final step they were inspected visually and under 100 x magnifications; their analysis indicated that the pans were free of any defects or blistering. This suggests that the coating invented by this method could produce a cookware with good corrosion resistant properties; however, the PTFE coating on the upper layer of the cookware could be damaged by the use of metal utensils.

As described in the previous section, the mechanical stability of a PTFE coating can usually be improved by mechanically treating the underlying substrate. As a modification to this procedure, Thomas et al. (2003) and Hayakawa (2007) invented new methods where abrasion resistant particles were directly introduced into the coating solution. In the method invented by Thomas et al. (2003), an inorganic filler film hardener containing large ceramic particles was added into fluoropolymer coating compositions; the authors suggest that the ceramic particles can prevent the abrasive action on the non-stick coating and hence protect the coating from subsequent removal. The cookware produced by this method was subjected to different types of abrasion tests (Thomas et al. 2003); the cookware showed lower coating loss (weight loss and thickness loss) than the conventional PTFE coated cookware. In the method developed by Hayakawa (2007), the cookware consists of an undercoat and an overcoat where the undercoat consists of a primer coating solution with diamond particles added into it, and the overcoat consists of a fluoropolymer coating solution containing ceramic particles of inorganic film hardener. The coated cookware was subjected to different types of abrasion tests, accelerated in-home abuse test and release tests. In the release tests, eggs were fried on the frying pan and they were lifted using a metal spatula; the ease with which the egg sled off the frying pan was assessed by a subjective release rating from 0 to 5. The author reported that the cookware was found to have good abrasion resistance and non-stick properties. However, in this type of cookware the majority of the coated surface consists of PTFE material which could be damaged by the use of metal utensils.

A method of forming a non-stick coating from a metal-ceramic impregnated layer was described by Becker (1980) and Groll (2009). Becker (1980) produced a non-stick coating by fabricating a porous ceramic layer onto the substrate by a sintering technique followed by filling the pores with a silicone resin. Groll (2009) developed a process where a metal-ceramic material such as chromium oxide or titanium oxide was applied with a controlled porosity of volume 5-15% onto a stainless steel substrate by a plasma spraying process. The pores were then sealed by a low viscosity silicone resin; the process was carried out under vacuum in order to completely fill all the pores with the silicone material. In the final step, the protruding peaks were removed by a mechanical polishing process in order to achieve a smoother surface for the final cookware. The frying pans coated by this method were subjected to cooking tests with a standard pancake batter where 500 pancakes were baked to a golden brown colour; the author found out that the pancakes were released from the pans without sticking by means of a metal spatula. They also carried out experiments in which the pancakes were left to burn on the pans and the pans were then cleaned using water and detergent; the pans were found to be easy to clean. The same type of experiments was repeated with eggs and similar kind of results was found in this case too. The durability of the frying pan was tested by scratching the surface by a sharp-tipped knife with a hardened carbon steel blade; the surface of the pan was not found to be scratched. In both of the above mentioned inventions, good mechanical properties were achieved by the use of ceramics whereas the use of silicone offered good non-stick properties.

Ceramics are of interest in many applications due to their excellent chemical and wear resistance properties. Cookware coated with ceramics was invented by many authors (Faulkner, 2001; Groll, 2006; Nagaoka and Kanno, 1995). A cookware coated with titanium based ceramic was invented by Nagaoka and Kanno (1995) in which a titanium film was deposited onto the cookware substrate; thereafter, a film of titanium nitride (TiN) was deposited onto the titanium film by a physical vapour deposition process. The coated substrate was then heated in an oxygen atmosphere to form a thin layer of titanium oxide on the top of the titanium nitride film. The frying pan coated by this method was evaluated by comparing it to a Teflon coated pan and a normal stainless steel frying pan. The pans were used for frying fish sole and minced pork and after frying, the weight of the food deposits remaining on each pan was measured 100 times; the deposit weight was low for the titanium nitride pan compared to the Teflon coated and the stainless steel pan. The frying pans were also subjected to a scratch test by scrubbing them with wire brushes where the titanium nitride pan maintained a good shine without any scratches compared to the Teflon coated and the stainless steel pan. In our studies, titanium aluminium nitride (TiAlN) material was chosen instead of titanium nitride (TiN) since TiAlN material is harder and possesses better abrasion resistance than TiN (Santos et al. 2007).

A zirconium based ceramic coated cookware was invented by Faulkner (2001) and Groll (2006). In the process described by Faulkner (2001), a stainless steel surface was coated with a primer layer (thin layer of chromium or aluminium nitride); a zirconium nitride layer was then deposited onto the primer layer by a physical vapour deposition process. Groll (2006) invented a method where the substrate of the metal cookware was electro-polished to produce a high luster finish and thereafter coated with a zirconium nitride film by a physical vapour deposition process. In order to test the efficiency of the coated cookware, the zirconium nitride film was deposited on two stainless steel frying pans with two different levels of roughness, after which they were compared to the bare uncoated stainless steel frying pan by different experiments; they were subjected to cooking tests with egg and baked beans followed by a scrape and wash test where a subjective rating from a scale of 1 to 5 was assigned based on their release and cleaning properties. The zirconium nitride film deposited on a smooth stainless steel substrate was found to have good release and cleaning properties; the properties were maintained even after 60 scrape and wash test trials. The ceramic coated cookware was found to have better release along with good scratch, wear and corrosion resistance properties.

In our studies, we aimed to find a material with high bonding energy similar to the PTFE material since PTFE's unique non-stick properties stem from the high bond energy between the carbon and fluorine atom in the PTFE molecule. Hence, Professor Per Møller, DTU Mechanics selected specific molecules and carried out thermodynamic calculations for them in order to calculate the Gibb's free energy (ΔG) required to break the bond between their atoms; the calculations were carried out using a software programme, HSC Chemistry 5.0 (http://www.chemistry-software.com/general/HSC_version5.html). He found that the Gibb's free energy (ΔG) required to break the bond between the zirconium and oxygen atom was higher than the Gibb's free energy (ΔG) required to break the bond between the carbon and fluorine atom in PTFE as shown in Table 2.1; the calculations are taken as an indicative only because in the first case ΔG is associated with the breakage of one covalent C – F bond whereas in the other two double bonds between zirconium and oxygen. The bond energy of zirconium oxide suggests that the zirconium oxide material is very inert and hence, any reaction between the food components and the zirconium oxide surface could not take place during the frying process, which is expected to result in good non-stick and cleaning properties. Zirconium based coatings, such as zirconium oxide and zirconium nitride were therefore chosen for our studies based on the bond energy between zirconium and oxygen; zirconium nitride also forms zirconium oxide on the outer layer of the surface when it comes into contact with the atmosphere.

Table 2.1 Bond energy calculations

Surface Material	T (^oC)	ΔG (kcal)
PTFE $CF_{4(g)} = CF_{3(g)} + F_{(g)}$	0	119
	100	115
	200	111
	300	107
Zirconium Oxide $ZrO_{2(s)} = Zr_{(s)} + O_{2(g)}$	0	250
	100	246
	200	241
	300	236

A quasicrystalline material is defined as a special kind of metallic material that possesses long range positional order but non-crystallographic orientational order (Dubois 2000; Goldmann and Widom, 1991; Van Blaaderen 2009). The use of a quasicrystalline material for cookware was first demonstrated by Dubois et al. (1994); it was first commercialized by Trademark Cybernox, Sitram, France. Quasicrystalline, being a material widely used for its good non-stick properties (Rivier et al. 1993; Minevski et al. 2009), was also selected for our studies.

In our studies, the different materials selected and tested were traditional food contact surfaces (aluminium and stainless steel), PTFE, silicone (coated on anodized aluminium), quasicrystalline and different ceramic coatings such as titanium aluminium nitride, zirconium oxide and zirconium nitride with two different levels of smoothness. A PTFE coated surface was included in all our tests since it is easier to recognize the non-stick properties of different surfaces in comparison to PTFE.

CHAPTER 3
MANUFACTURE OF COATINGS AND THEIR CHARACTERIZATION

3.1. Surface modification techniques

3.1.1. Ceramics

Three different types of ceramic coatings: zirconium oxide (ZrO_2), zirconium nitride (ZrN), and titanium aluminium nitride (TiAlN) were chosen for the purpose. They were all deposited on two different stainless steel discs of 90 mm in diameter with two different levels of roughness: unpolished stainless steel (UP 316 SS) and electro-polished stainless steel (EP 316 SS). These ceramic coatings were manufactured by Physical Vapor Deposition (PVD) process where DC magnetron sputtering is the technique employed to deposit the coating as described in the following section. The ceramic coatings were provided by Danish Technological Institute, Aarhus, Denmark.

Physical Vapour Deposition

A physical vapour deposition process can be defined as an atomic deposition process in which a material is vaporized from a solid or liquid source in the form of atoms or molecules, transported in the form of a vapor through a vacuum or low pressure gaseous or plasma environment to the substrate where it condenses (Mattox, 1998).

DC Magnetron Sputtering

Sputter deposition means that the physical sputtering process, the process in which the target surface is vaporized by momentum transfer from bombarding energetic atomic sized particles, is employed for deposition of the particles on the substrate surface. In DC magnetron sputtering, the sputtering target is employed as the cathode electrode and the substrate to be deposited is treated as the anode which is usually at ground potential. In this case, the electrons from the cathode are made to stay closer to the target surface by application of a magnetic field; the electrons are made to circulate on a closed path by proper arrangement of the magnets. High density plasma is created by the high flux of electrons, and ions extracted from the generated plasma are used to sputter the target material.

Reactive sputter deposition

Reactive sputter deposition involves sputtering from an elemental source in a partial pressure of a reactive gas such as oxygen or nitrogen. The oxygen and nitrogen generally have low atomic masses (N=14; O=16) and cannot be used as such in sputtering. Hence, a heavier inert gas such as argon is normally used to assist in the sputtering process. In this case, zirconium oxide (ZrO_2) and zirconium nitride (ZrN) coatings were deposited by using metallic zirconium as the source material (sputtering target) and oxygen and nitrogen as the reactive gases. A titanium aluminium nitride (TiAlN) coating was deposited by employing titanium and aluminium as metallic sources (sputtering target) with nitrogen as the reactive gas. A cathode power source (sputtering target) which is 88 x 200 mm in length with a voltage of 400 V (3000 W) was employed to produce the coatings.

Substrate surface morphology

The morphology of the substrate surface affects the properties of the deposited film. Smooth surfaces yield more dense PVD coatings than rough surfaces due to the lack of "macro-columnar morphology" resulting from geometrical shadowing of features on the substrate surface (Mattox, 1998). There are two ways in which a surface can be polished:

(i) Mechanical Polishing

This technique is commonly used to produce smooth surfaces and makes use of a hard surface material abrading against the material to be polished. In case of brittle materials, this process can create surface flaws which will weaken the interface when the film is deposited.

(ii) Chemical Polishing

A chemical polishing process produces a smooth surface by eliminating the peak points on the surface layer. An electro-polishing process is a commonly used method to produce smooth surfaces on some metals, which is described as follows:

Electropolishing

Electropolishing is an electrolytic process, used for removing part of the surface, in which the material removal takes place ion by ion (Kosmac, 2010). It is a commonly employed process in the industry to reduce the micro-roughness of metallic substrates: aluminium and stainless steel (Kosmac, 2010; Moller and Nielsen, 2010). The material resulting from the electropolishing process has a smooth and luster finish. In order to carry out the electropolishing process, a concentrated solution of sulphuric acid and phosphoric acid is used as an electrolyte and the process is carried out at a temperature of $60^{o}C$ with a current of 35 A/dm^2 for five minutes.

3.1.2. Quasicrystalline

The quasicrystalline coating material tested in this work consists of iron (Fe), chromium (Cr) and aluminium (Al) as the main constituents. The coating was deposited on stainless steel discs (90 mm in diameter) by a High-velocity oxy-fuel (HVOF) flame spray method (Shaitura and Enaleeva, 2007 Huttunen-Saarivirta et al. 2003) as described in the following section. The coating was supplied by Saint-Gobain, France and the thickness of the coating was reported to be 300 ± 25 µm.

HVOF (High Velocity Oxy-Fuel)

Thermal spraying is a coating process in which a solid coating material is melted or softened and sprayed with a significant velocity onto a surface. The process employs a fuel (i.e., propylene, hydrogen, propane, kerosene) /oxygen mixture in a combustion chamber. The metal powder is continually fed into the spray gun using a carrier gas (argon). The combustion process melts the metal powder and propels it at high speeds (in the range of 500 - 600 m/s) towards the surface of the part to be coated; the high speed of the spray produces a coating upon impact. The sprayed material is immediately cooled down from its molten or partially molten state to substrate temperature, which allows the coating to adhere to the substrate by mechanical or physical bonding.

3.1.3. PTFE (Polytetrafluoroethylene)

Polytetrafluoroethylene was coated on aluminium (Al Mg 5754) and stainless steel discs (90 mm in diameter) by the spray coating technique as described in the following section. The substrate was aluminium sand blasted before the coating application. The coating layer consists of a base coat and a top coat in which the base coat was cured at a temperature below 100^{o}C for 2-4 minutes and the top coat was cured at a temperature above 400° C for 10-15 minutes. The coating was supplied by Whitford Worldwide, Brescia, Italy. The thickness of the coating was reported to be 25 ± 10 µm.

Spray technique

Spray technique can be defined as “a coating technique in which a liquid coating material is sprayed onto the top of a substrate followed by a physical drying or a thermal curing process”. Physical drying involves evaporation of solvent from the coated substrate at room temperature, whereas the thermal curing process involves heat treatment of the coated substrate for a specific period of time.

The substrate is normally sandblasted before the coating process in order to improve the adhesion of coating to the substrate. Coatings of varying thickness in the micrometer range can be produced by this technique.

3.1.4. Silicone

The silicone rubber ELASTOSIL® E 60 was used for making the silicone coating. The silicone was coated on anodized Al-Mg 5754 aluminium substrate (for anodizing process, refer to the next section) by spray coating technique as described above at Accoat A/S, Kvistgard, Denmark. The ratio of ELASTOSIL® E 60 and acetone in the coating solution was 1:4. It was sprayed onto the top of the anodized aluminium disc (90 mm in diameter). The coated panel was finally cured by oven baking at a temperature of 200^{o}C for 5 minutes where a final coating thickness of 19 ± 2 µm is achieved.

Anodising

Anodising is an electrolytic process in which an artificial thickening of the aluminium oxide layer takes place, an oxidation reaction takes place at the anode and a reduction reaction takes place at the cathode in accordance with the following equation:

Anodic reaction : $2Al + 3H_2O \rightarrow Al_2O_3 + 6H^+ + 6e^-$ (1)

Cathodic reaction : $6H^+ + 6e^- \rightarrow 3H_2$ (2)

A stainless steel plate was used as the cathode whereas the aluminium substrate which was to be anodized was made as the anode in the electrolytic process and hence the name anodising. The aluminium substrate (Al Mg 5754) was first subjected to etching by a 10% sodium hydroxide solution and then deoxidized by soaking in a 50% nitric acid solution. The substrate was then anodized in a sulphuric acid bath (3.5mol/l) with standardized anodising conditions, voltage of 20 V and a current of 2 A/dm^2, for a period of 20 minutes at room temperature. The anodized layer thickness was found to be 23 µm.

3.1.5. Sol-gel coating

Sol-gel is a wet-chemical technique for synthesizing coatings where a system of colloidal particles in a solution (sol) becomes a macroscopic material (gel). The sol-gel reaction consists of two chemical reactions: hydrolysis and condensation reaction; the sol is produced by hydrolysis reaction whereas the condensation reaction produces the macroscopic gel formed on the substrate producing a thin film. Typically, organoalkoxysilanes such as tetraethoxysilane (TEOS), 3-glycidoxypropyltrimethoxysilane (GPTMS) etc., and metal alkoxides such as zirconiumtetrapropoxide (TEOS), titaniumtetrapropoxide, etc., are used as organic and inorganic precursors in the preparation of the hybrid sol-gel coatings (Zheludkevich et al. 2006). The hydrolysis and condensation reactions of the metal alkoxides are very fast and must be controlled by the use of inhibitors such as diketones, diethylene-glycol, carboxylic acids which inhibit the condensation reaction (Balamurugan et al. 2003). The sol-gel coating procedure employed in the present study is described in Appendix I.

The coatings produced by the sol-gel technique in the present study were unsuccessful because a good adhesion between the coating and the substrate cannot be attained by this method. If a coating needs to be tested for its properties, especially non-stick performance, there should be sufficient adhesion between the coating and the substrate; otherwise, the coating could detach from the substrate during testing. In such cases, it is not possible to evaluate their performance and these sol-gel coatings were therefore abandoned for further analysis and testing.

3.2. Surface Characterization

3.2.1. Surface topography

Roughness

Roughness is defined in the British Standard (BSI BS 1134-1) as “The irregularities in the surface texture which are inherent in the production process but excluding waviness and errors of form”. The nature and degree of surface roughness is termed as the morphology of a surface (Mattox, 1998). Surface roughness parameters derived from surface profile graphs can measure the vertical variation (amplitude), horizontal variation (spatial) and others (a combination of amplitude and spatial components) (Stout, 1981). Surface topography is mainly characterized by amplitude parameters (Gadelmawla et al. 2002; Whitehead and Verran, 2006). The parameters such as R_a, R_z,

R_q, R_t and R_p are examples of amplitude parameters. R_a stated in µm is the most widely used descriptor for surface roughness (Kuisma et al. 2007; Määtta et al. 2007; Verran et al. 2000). R_a is expressed as the average height or depth of the peaks above and below the average centerline of a surface (Kuisma et al., 2007). R_a will not give any information regarding the shape of the surface (Stout, 1981); but, can give useful information regarding the variations in the height (Gadelmawla et al. 2002; Whitehead and Verran, 2006).

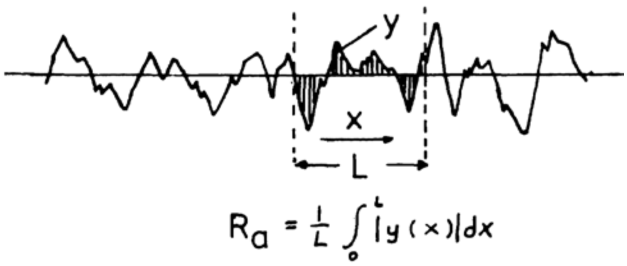
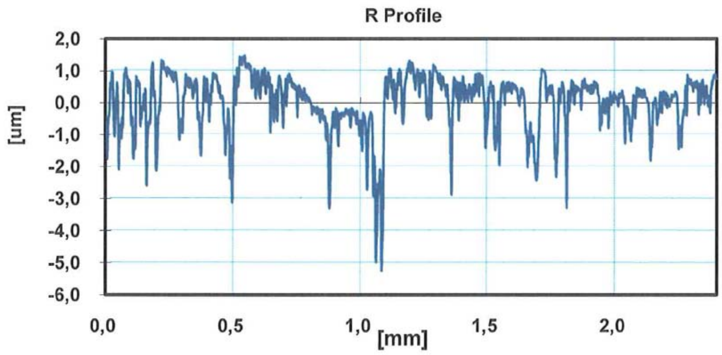
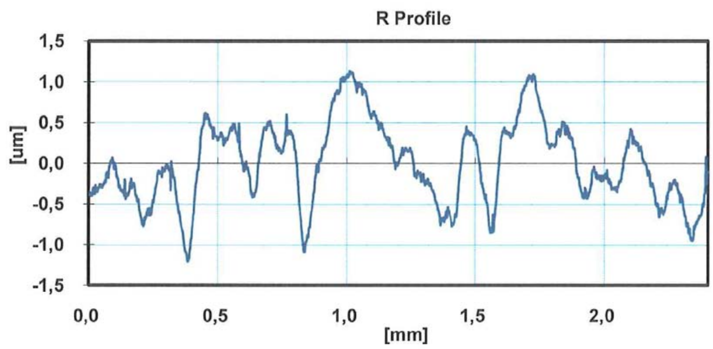


Figure 3.1. Schematic and mathematical description of R_a (Stout, 1981)



(a)



(b)

Figure 3.2. Roughness profiles of a ceramic (TiAlN) coated on substrates with two different surface treatments (a) unpolished stainless steel (b) electropolished stainless steel

Table 3.1. The surface code, surface description, coating method and roughness R_a values of the different surfaces

Surface Code	Description	Coating method	Roughness Value Ra (µm)
UP 316 SS	Unpolished 316 Stainless steel	None	0.44 ± 0.04
TiAlN (UP 316 SS)	Titanium Aluminium Nitride coated on UP 316 SS[a]	Physical Vapour Deposition	0.72 ± 0.08
TiAlN (EP 316 SS)	Titanium Aluminium Nitride coated on EP 316 SS[b]	Physical Vapour Deposition	0.47 ± 0.06
ZrN (UP 316 SS)	Zirconium Nitride coated on UP 316 SS[a]	Physical Vapour Deposition	0.68 ± 0.08
ZrN (EP 316 SS)	Zirconium Nitride coated on EP 316 SS[b]	Physical Vapour Deposition	0.27± 0.04
ZrO_2 (UP 316 SS)	Zirconium Oxide coated on UP 316 SS[a]	Physical Vapour Deposition	0.67 ± 0.08
ZrO_2 (EP 316 SS)	Zirconium Oxide coated on EP 316 SS[b]	Physical Vapour Deposition	0.40 ± 0.06
QC (Al, Fe, Cr)	Quasicrystalline coated on UP 316 SS[a]	High Velocity Oxy-Fuel	0.30 ± 0.07
PTFE	Polytetrafluoroethylene coated on UP 316 SS[a]	Wet spray	0.50 ± 0.06
Silicone	Silicone rubber ELASTOSIL® E 60 coated on anodized aluminium	Wet spray	0.13 ± 0.03

a - Unpolished 316 stainless steel

b - Electropolished 316 stainless steel

Measurement of surface roughness

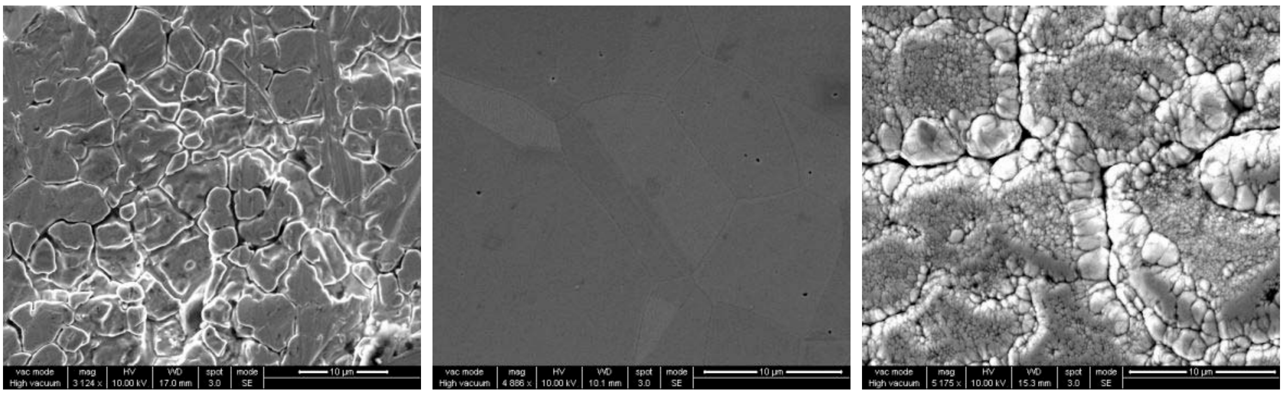
Stylus type instruments are most widely used for surface roughness measurements (Kuisma, 2006). Two types of surface profilometers are in use (Poon and Bhushan, 1995): (i) Contact-type profilometer in which a stylus is in contact with the surface and moves over the surface (ii) Non-contact type profilometer in which the stylus is not in contact with the surface. Roughness parameters were measured by using contact-type profilometer which is described in the following section.

Contact-type profilometer

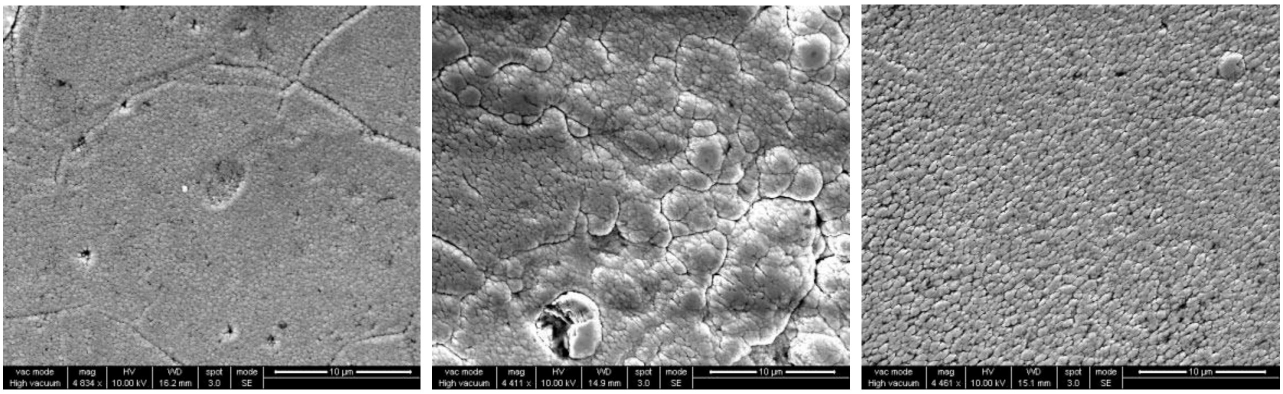
The two-dimensional roughness profile of the materials was measured using a Surftest SJ-201 Surface Roughness Tester (Mitutoyo, USA) according to Japanese Standards Association JIS B0601-1982. The 5 µm diamond stylus traverses on the test material at a speed of 0.25 mm/s. The downward force of the stylus was 4 mN and the measurement range was 350 µm. The cut-off length was 0.8 mm. Before each measurement, the instrument was calibrated using a reference work piece. The results were expressed as the mean of ten readings for each material.

Scanning Electron Microscopy

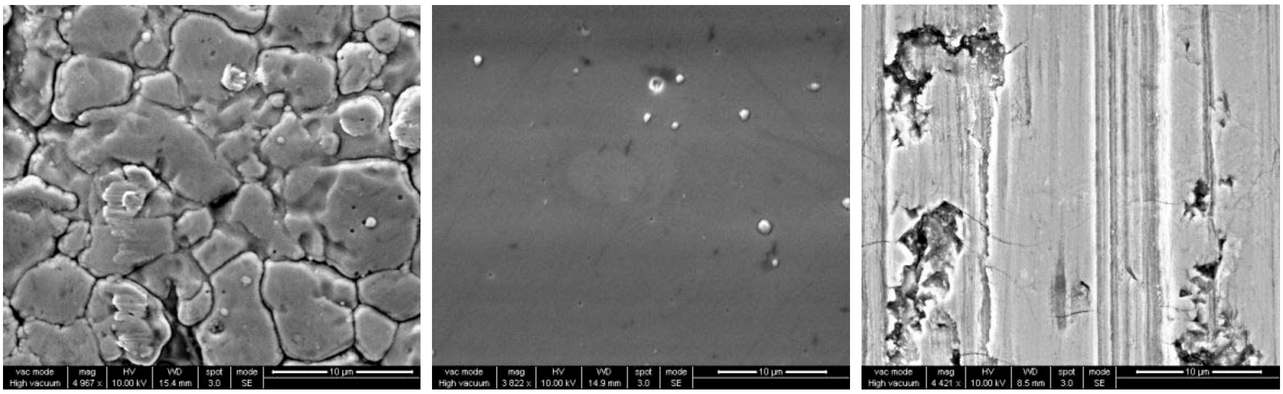
Scanning Electron Microscopy is a widely used technique to characterize the surface topography. The images in scanning electron microscopy are produced by detection of secondary electrons which are emitted from the surface due to excitation by the primary electron beam. An accurate measurement of the surface topography over nanometer to millimeter range is possible by the use of SEM (Kuisma, 2006; Watt, 1997). Scanning electron microscopy is very useful to visually observe the topographical features; however, it is not possible to obtain quantitative data about the height of surface features as in profilometry techniques (Sherrington and Smith, 1988). The scanning electron microscope (FEGSEM 200F) was used to study the morphology of different surfaces as shown in Fig 3.3. The photomicrographs were taken with a magnification of 10 µm using an accelerating voltage of 10 kV for all the examinations except for polymers where an accelerating voltage of 1 kV is used to obtain good pictures.



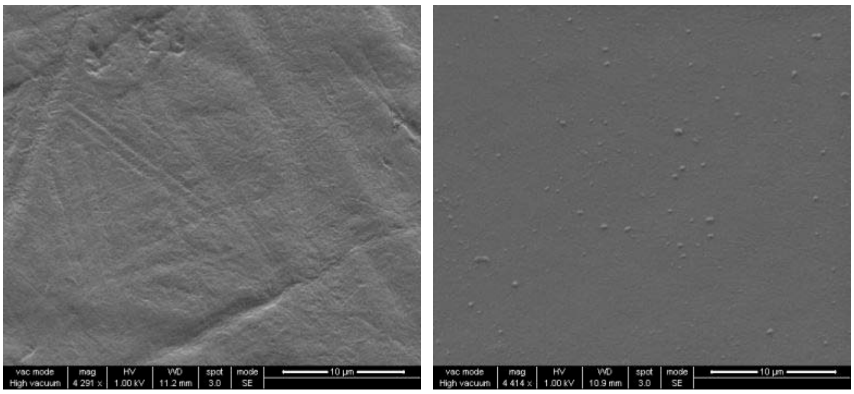
(a) (b) (c)



(d) (e) (f)



(g) (h) (i)

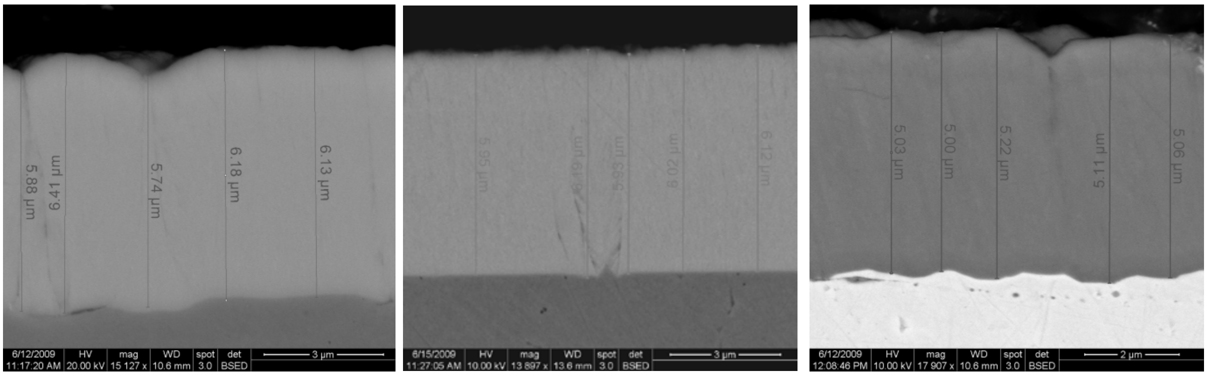


(j) (k)

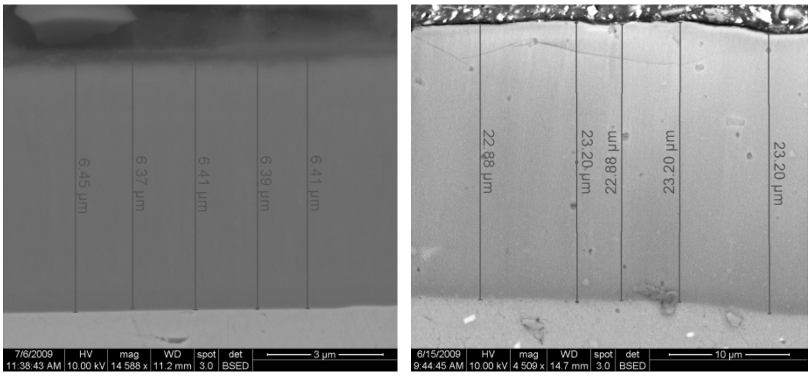
Fig 3.3. SEM photomicrographs of different surfaces (a) stainless steel (b) electropolished stainless steel (used as a substrate for depositing ceramic coatings) (c) TiAlN (UP 316 SS) (d) TiAlN (EP 316 SS) (e) ZrN (UP 316 SS) (f) ZrN (EP 316 SS) (g) ZrO_2 (UP 316 SS) (h) ZrO_2 (EP 316 SS) (i) QC (Al, Fe, Cr) (j) PTFE (k) Silicone

Coating thickness measurements

In order to find the thickness of different coatings coated on metal substrates, the samples were cut perpendicular to the coating and embedded in epoxy resin. Struers grinding machine was used to grind and polish the samples to 4000 SiC finish. The coating thickness values were then measured using scanning electron microscope (FEGSEM 200F); for ex. the coating thicknesses were found to be 6 µm for ZrN, 5-6 µm for TiAlN and 23 µm for anodic oxide layer (used as a substrate) as shown in Figure 3.4.



(a) (b) (c)



(d) (e)

Figure 3.4. Cross-sectional view of different surfaces with coating thicknesses of (a) ZrN (UP 316 SS) (b) ZrN (EP 316 SS) (c) TiAlN (UP 316 SS) (d) TiAlN (EP 316 SS) (e) Anodized aluminium oxide layer

3.2.2. Contact Angle

The angle formed by the solid-liquid interface and the liquid-vapor interface is called as the contact angle between a liquid drop and a solid surface (Handojo et al. 2008). The contact angle, θ, of a liquid drop on a flat surface is related to the interfacial energies of solid - liquid (γ_{SL}), liquid - vapor (γ_{LV}) and solid - vapor (γ_{SV}) by Young's equation (Bargir et al. 2009; Handojo et al. 2008; Sun et al., 2007):

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos\theta \tag{1}$$

If the measured contact angle with water is greater than 90°, the material is said to be hydrophobic and the material is said to be hydrophilic in nature if the contact angle value with water is less than 90°.

Rhee et al., 1971 found that the cosine of the contact angle of a liquid metal on a ceramic surface shows a linear increase with increase in temperature in accordance with the equation (2). Fox et al., 1955 found that the cosine of the contact angle of an organic liquid on high energy surfaces also shows a linear increase with increase in temperature.

$$\cos\theta = A + BT\ (^{o}C) \tag{2}$$

where A is a constant and B is the slope.

The contact angle of a liquid drop on a rough surface follows the Wenzel equation (Veeramasuneni et al., 1997):

$$\cos\theta_a = r\cos\theta \tag{3}$$

where θ_a - apparent contact angle (measured through a microscope), r - surface roughness ratio(r = a/A = (da/dA ≥ 1), a - actual area of surface, A - apparent area or geometrical area of the surface, θ - intrinsic contact angle.

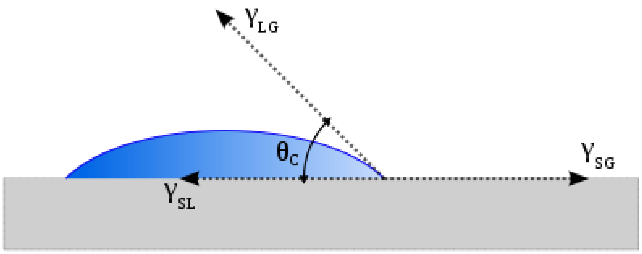


Figure 3.5. Contact angle of a liquid sample on a solid surface

Contact angle measurements

Electrocleaning process

Electrocleaning process was performed in order to clean different surfaces prior to the contact angle measurements. Electrocleaning is an electrolytic process conducted by passing direct current through an alkaline electrolyte. There are two types of electrocleaning:

(i) anodic: if the material to be cleaned is connected to the anode and

(ii) cathodic: if the material to be cleaned is connected to the cathode.

Electrocleaning process is effective in removing the organic soils, dirts, solid particles and oxides adhered to the surface since it combines the effect of chemical cleaning (soaking in alkaline solution) and mechanical cleaning (provided by gas bubbles). Cathodic cleaning was chosen for the purpose because it is more effective than anodic cleaning due to the more intensive hydrogen gas liberation according to the equation:

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2 \quad (4)$$

The cleaning process was carried out by passing a current of 10 amperes through the electrolyte (20 g/l sodium hydroxide solution) for two minutes. In order to remove the alkaline residues remaining on the surface after the electrocleaning process, the surface was immersed in a dilute solution of sulphuric acid for a period of 1 - 2 minutes. The surface was then rinsed with running water and dried using a hair dryer before each measurement. These conditions were standardized and found to be optimal for this experiment.

Sessile drop technique

Sessile drop technique is a widely used method for contact angle and surface tension measurements. The sessile drop instrument (Dataphysics OCA-20, DataPhysics Instruments GmbH, Filderstadt, Germany) was employed to measure the contact angle. This instrument is equipped with a CCD video camera having a resolution of 752 x 582 pixels which can take 50 pictures per second and a temperature controlled chamber ranging between -10 and 400 o C with manual or electronic dosing units. The surface which is to be characterized was placed in the chamber and measurement of contact angle was performed at room temperature; for measurements at high temperature, the surface was heated to the required temperature. A 4 µl drop of water or olive oil was placed on the surface and the image of the drop was captured immediately. The contact angle with an accuracy of ± 0.1 o is calculated from the drop image by the image analysis software integrated in the system. Each experiment is repeated for five times by placing new drops on different points on the surface and the reported contact angle values are the average of five repetitions.

Table 3.2. Contact angle (mean of five repetitions) of water and olive oil on different surfaces at room temperature

Surface Material	Contact Angle (^{o})	
	Water	Oil
UP 316 SS	57.7 ± 0.4	17.4 ± 0.3
TiAlN (UP 316 SS)	54.4 ± 0.2	14.0 ± 0.9
TiAlN (EP 316 SS)	48.5 ± 0.6	16.0 ± 0.5
ZrN (UP 316 SS)	54.7 ± 0.8	9.6 ± 0.4
ZrN (EP 316 SS)	41.9 ± 1.1	15.5 ± 0.3
ZrO_2 (UP 316 SS)	65.2 ± 0.7	8.5 ± 0.5
ZrO_2 (EP 316 SS)	56.1 ± 0.3	15.8 ± 0.4
QC (Al, Fe, Cr)	108.3 ± 0.5	41.8 ± 0.9
PTFE	117.2 ± 0.4	67.8 ± 0.8
Silicone	117.3 ± 0.5	75.3 ± 0.3

The contact angle measurements with water show that the surfaces: QC (Al, Fe, Cr), PTFE and silicone are hydrophobic in nature since the measured contact angle values of water on these surfaces were greater than 90^o. The other surfaces: UP 316 SS, TiAlN (UP 316 SS), TiAlN (EP 316 SS), ZrN (UP 316 SS), ZrN (EP 316 SS), ZrO_2 (UP 316 SS) and ZrO_2 (EP 316 SS) are hydrophilic in nature since their contact angle values with water were less than 90^o.

3.2.3. Wear

Wear is defined as damage to a solid surface, generally involving progressive loss of material, due to relative motion between the surface and a contacting substance or substances (ASTM G-40). A different classification of wearing mechanisms has been proposed by different authors: Meigh (2000) used three classes: abrasive, adhesive, delamination wear; Kimura et al. 2002 has proposed three classes: abrasive, adhesive, corrosive wear; Gahr (1988) proposes four classes: abrasive, adhesive, surface fatigue and tribochemical reaction. The interaction between an abrader and the material being abraded can be divided into microploughing, microcutting, microfatigue and microcracking. However, wear is a complex process which might involve several mechanisms and hence due to the possible interaction between these mechanisms, the obtained data is difficult to interpret and use (Li et al. 1999). Eventhough, both thickness and mass loss measurements were widely used to examine the wear of materials analysis of the mass loss of materials is an important indicator of wearing (Kuisma, 2006).

Wear testing apparatus

The abrasive wear experiments were performed at room temperature in air using an abrasive wear tester (ABR-8251-1) shown in figure 3a. The function of the apparatus is in accordance with ISO 8251 standard. A glue transferring tape (3M type 465, 12 mm) is attached to the abrasive wheel on which an abrasive tape (mesh 320, SiC) is mounted; subsequently the wheel is screwed back on tightly. The sample mounting board has a slit, as shown in figure 3b, through which the abrasive wheel gets in contact with the sample. The preferred load can be applied by placing appropriate weight on the lever arm. The board move back and forth to remove the surface material, resulting in a test area of 12 x 30 mm. The board makes a rotation at the end position to expose the fresh tape each time when the wheel comes into contact with the sample.

Experimental procedure

Before each test, the test sample is cleaned with H_2O and high-pressure air, thereafter with ethanol and warm air (hair dryer). The sample is weighed before the start of the test using a balance with a resolution of 0.1 milligram. The pressure applied between the surface and the abrasive wheel is 4.9N=500g, corresponding to the standard. A board speed of 40 RPM and an abrasive wheel rotation of 400 and a classic sequence of abrasion intervals: 50, 100, 200, 400, 800 and 1200 double strokes were chosen in accordance with the standard. After completion of each double stroke, the sample is weighed to determine the mass loss. Since the ceramics show a tendency to absorb moisture from the atmosphere, troubles were encountered in finding their mass loss values after each double stroke. Hence, the ceramic coated plates were heated at $100^{o}C$ in an oven for 10 minutes before measuring their mass loss values.

(a)

(b)

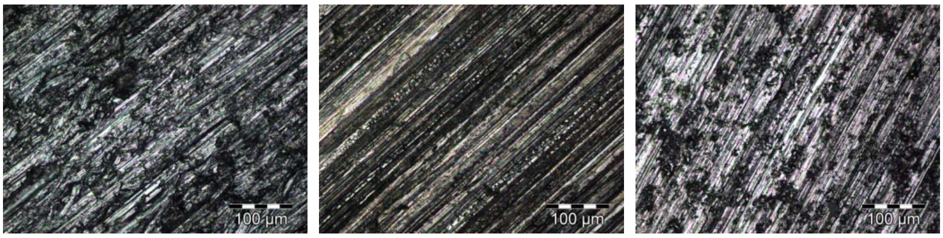
Figure 3.6. (a) Schematic view of the abrasive wear testing equipment (b) Top view of the apparatus with the fixture open

Table 3.3. Mass loss of different surface materials subjected to abrasive wear

Double Strokes /Surface Material	Average mass loss (three repetitions) in milligrams					
	50	100	200	400	800	1200
UP 316 SS	1.58	3.1	6.21	11.26	22.76	34.16
Al Mg 5754	2.57	4.05	7.34	18.16	46.16	74.71
TiAlN (UP 316 SS)	0.01	0.04	0.04	0.06	0.13	0.20
TiAlN (EP 316 SS)	0.04	0.17	0.21	0.21	0.25	0.31
ZrN (UP 316 SS)	0.15	0.15	0.20	0.27	0.38	0.52
ZrN (EP 316 SS)	0.16	0.21	0.28	0.32	0.54	0.76
ZrO_2 (UP 316 SS)[1]	2.11	-	-	-	-	-
ZrO_2 (EP 316 SS)[2]	1.49	-	-	-	-	-
QC (Al, Fe, Cr)	3.42	6.78	11.49	19.49	34.19	47.23
PTFE[3]	7.59	13.32	22.14	33.28	-	-
Silicone[4]	7.03	13.54	21.68	35.96	-	-

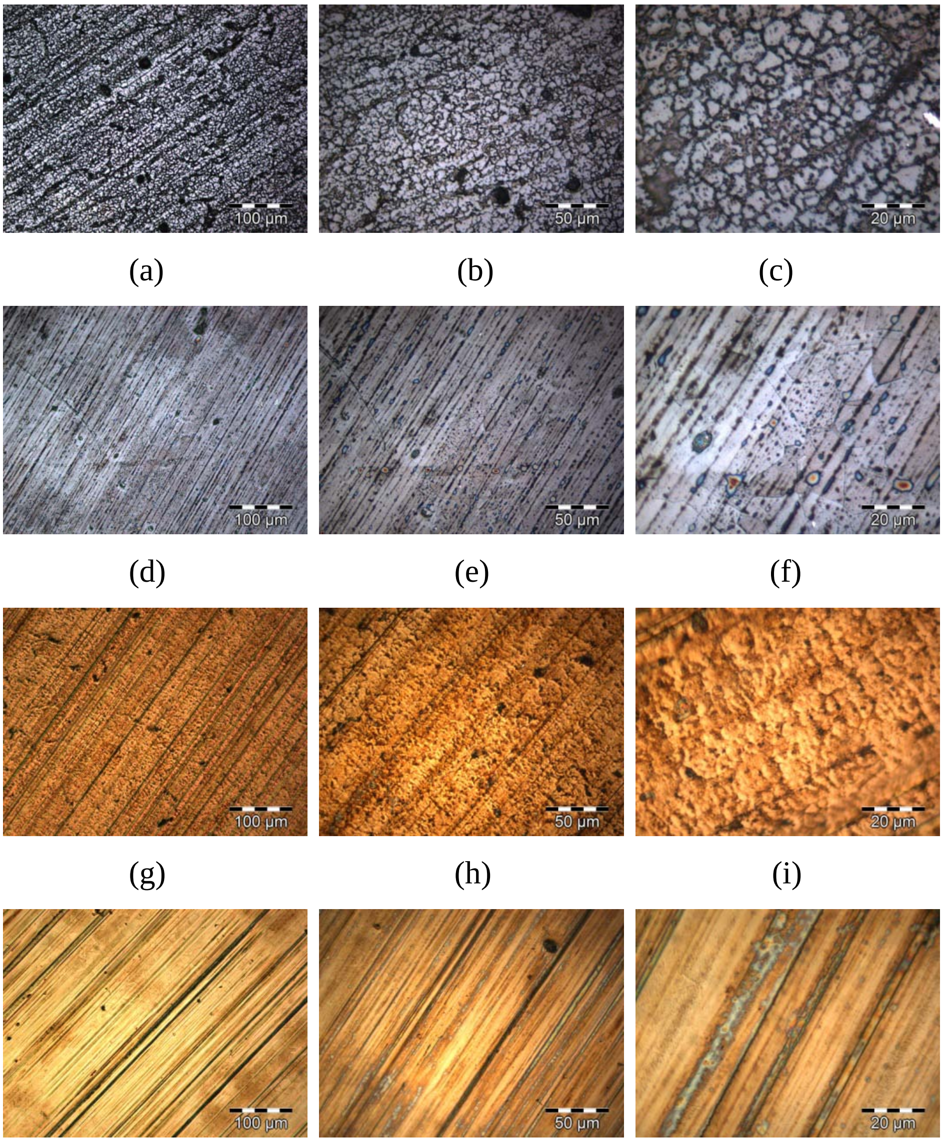
1, 2 - Substrate is exposed after 50 double strokes

3, 4 - Substrate is exposed after 400 double strokes



(a) (b) (c)

Figure 3.7. Optical micrographs of the wear tracks produced on (a) aluminium (b) stainless steel and (c) QC (Al, Fe, Cr) after 1200 double strokes



(a) (b) (c)

(d) (e) (f)

(g) (h) (i)

(j) (k) (l)

Figure 3.8. Optical micrographs of the wear tracks produced on (a) - (c) TiAlN (UP 316 SS); (d) - (f) TiAlN (EP 316 SS); (g) - (i) ZrN (UP 316 SS) and (j) - (l) ZrN (EP 316 SS) after 1200 double strokes

Table 3.3 shows the mass loss of different materials which are subjected to abrasive wear. As shown in the table, the mass loss of aluminium after 1200 cycles is twice than the mass loss of stainless steel. This shows that the wear resistance of aluminium is poorer than stainless steel. This is in accordance with the practical experience in household kitchen where the aluminium utensils usually abrade or wear quickly than the stainless steel utensils during mechanical cleaning process. The polymers (PTFE and silicone) cannot resist the whole 1200 cycles since the substrate material (stainless steel) is revealed after 400 cycles. This confirms the poor wear resistance of polymers which is responsible for their poor attention in specific applications. The quasicrystalline coating showed higher mass loss compared to stainless steel and hence poorer wear resistance than that of stainless steel. This is in accordance with that of Matthews et al. 1999 who reported that the quasicrystalline coatings exhibit higher wear rate than that of metallic materials. The authors also suggest that the low coefficient of friction of quasicrystalline materials does not necessarily mean a low wear rate. The results indicate that titanium aluminium nitride (TiAlN) has got the best wear resistance among all the materials tested. This is in accordance with many studies which reported the best wear properties of titanium nitride based coatings (Budinski, 2004; Rickerby and Burnett, 1987). Next to TiAlN, zirconium nitride (ZrN) has got the best wear properties. The extremely low mass loss values for TiAlN and ZrN coatings even after 1200 double strokes shows that the coating is very hard to be weared by the SiC paper. The ceramics deposited on polished steel showed higher mass loss compared to ceramics deposited on unpolished steel. Since the mass loss is too small for the ceramics, accurate prediction of wear performance becomes difficult. The nano-layer coating zirconium oxide (ZrO_2) showed a very poor wear resistance among the different materials analyzed since the substrate material (stainless steel) is revealed within 50 cycles. This could be due to a very thin layer of the coating (0.6 µm) which cannot resist the abrasive action produced by the test procedure.

Figures 3.7 and 3.8 show the wear tracks produced on different surfaces where the wear tracks of ptfe, silicone and zirconium oxide ceramics are not shown since the substrate material is exposed during the wear tests. The optical micrographs suggest that the wear is taking place mainly by abrasion. The removal of material by plowed furrows is characteristic of scratching abrasion; the substrate is plastically deformed into furrows aligned with the direction of the abrasive grains (Budinski, 2004). This mechanism is found to be dominating in case of metals (stainless steel, aluminium) and quasicrystalline coating. Wear resistance of material is closely related to its micro hardness, toughness, microstructure, defects in the coating, etc., (Wang et al. 2000); the presence of numerous defects (figure 3.2i) and brittle nature of the quasicrystalline coating (Dubois, 2000) could possibly result in poor wear resistance.

The wear tracks for ceramics shown in figure 3.7 illustrate that the wear scratches are sharper and deeper on ceramics coated on polished steel compared to the scratches on ceramics coated on unpolished steel. Figure 3.7c indicates that the zirconium nitride coating deposited on unpolished steel undergoes plastic deformation which is confirmed by the presence of grooves in the coating; whereas no such clear grooves can be seen in case of titanium aluminium nitride coating deposited on unpolished steel. Since the extent of wear is affected by the microstructure of ceramics (Krishnamurthy et al. 2010), the differences in their microstructure could also contribute to the differences in their wear mechanisms. However, in certain cases one or several mechanisms can determine the wear resistance of the materials. When we observe the micrographs of ceramics coated on polished steel, it can be clearly seen that the substrate material (stainless steel) is exposed in some areas. there are two possibilities in this case (i) a more intimate contact between the smooth surface finish of the ceramics deposited on polished steel and the abrader can form local weld junctions which can result in galling (Meigh, 2000; Schumaker, 1977) (ii) adhesion between the coating and the electropolished smooth stainless substrate is weaker than the adhesion between the coating and the unpolished rough stainless substrate; an adhesive failure at the interface between the coating and the substrate is likely during the abrasive wearing process which could result in loss of material. This observation is in accordance with the higher mass loss values obtained for ceramics deposited on polished steel compared to ceramics deposited on unpolished steel.

Wear testing equipments and the test geometry should be selected in a way which can characterize the real circumstances as closely as possible (Møller and Nielsen, 2010). This particular method is chosen to better simulate the food frying conditions in which the frying surface material is often flat and frequently scratched by metal spatulas or metal scrapers where the surface material is expected to have high wear resistance. The results produced by this method gave good ranking of materials which corresponds with the practical experience. the tribology behavior of two surfaces depends on several factors including material of the rubbing surfaces, atmosphere, possible lubrication, contact pressure, sliding speed, temperature, etc., (Michalczewski et al. 1998) and hence, the wear of materials vary highly depending on the working conditions.

3.2.4. Friction

Friction is generally used along with wear for tribology characterization of surfaces. The co-efficient of friction is defined as "the ratio of the force required to move one surface over another to the total force applied normal to those surfaces" (ASTM D1894 -08). The co-efficient of friction is determined using material testing instrument (model LR 5K, Andertech Plastteknik A/S, Humlebæk, Denmark) in accordance with the standard ASTM D1894 - 08. A sled with a weight of 200 g is placed on the sample (63.5 x 63.5 mm) and the sample was moved against rectangular 316 stainless steel surface (25 x 13 mm) at a constant speed of 150 mm/min; there is no lubrication between the surfaces.

The static co-efficient of friction is calculated as follows:

$\mu_S = A_S/B$

μ_S - static co-efficient of friction

A_S - initital force required to start the motion in g

B - sled weight in g

The dynamic co-efficient of friction is calculated as follows:

$\mu_K = A_K/B$

μ_k - static co-efficient of friction

A_k - average force obtained during uniform sliding of the sample over the stainless steel surface in g

B - sled weight in g

Table 3.4. Co-efficient of friction (mean of five repetitions) of different surfaces measured by pulling against 316 stainless steel at room temperature

Surface Material	Static	Dynamic
Aluminium Al Mg 5754	0.47 ± 0.09	0.28 ± 0.05
UP 316 SS	0.65 ± 0.07	0.46 ± 0.04
TiAlN (UP 316 SS)	0.64 ± 0.14	0.28 ± 0.11
TiAlN (EP 316 SS)	0.98 ± 0.07	0.62 ± 0.10
ZrN (UP 316SS)	0.61 ± 0.03	0.37± 0.04
ZrN (EP 316 SS)	0.81 ± 0.10	0.54 ± 0.05
ZrO_2 (UP 316 SS)	0.48 ± 0.02	0.28 ± 0.03
ZrO_2 (EP 316 SS)	0.84 ± 0.06	0.48 ± 0.05
QC (Al, Fe, Cr)	0.60 ± 0.11	0.32 ± 0.04
PTFE	0.43 ± 0.06	0.16 ± 0.01
Silicone	0.52 ± 0.05	0.34 ± 0.02

In general, the friction force can be considered as the sum of two contributions: (i) abrasive contribution resulting from surface asperities deforming the counter surface (ii) adhesive contribution resulting from shearing of adhesive contacts (Axen et al.1996); adhesion is a dominating phenomenon for friction between the two materials (Maatta et al. 2001). The presence of contaminant layers can significantly affect the tribology of two materials in contact (Chung, 1992). The contaminants can act as a lubricant reducing the adhesion between two contacting surfaces (Määtta et al. 2001).

Table 3.4 shows the static and dynamic co-efficient of friction values for different surfaces measured by pulling against stainless steel at room temperature. Among the different materials tested, PTFE has got the lowest static and dynamic co-efficient of friction which could be due to its self-lubricating nature. The co-efficient of friction values for different ceramics (TiAlN, ZrN, ZrO_2) reveals that the ceramics coated on unpolished steel has got lower values than the ceramics coated on polished steel. This is in accordance with Myshkin et al. 1998 who suggested that the co-efficient of friction decreases with increase in surface roughness because increasing the surface roughness decreases the adhesion between two surfaces since it causes the contact to occur only at discrete points (Bhushan, 2003; Myshkin et al. 1998). Moreover, the differences in contaminant films on the surfaces could also give rise to difference in the measured frictional force.

As seen from tables 3.4 and 3.5, no definite correlation can be observed between the co-efficient of friction and wear of different materials (Meigh, 2000; Hutchings 1992). For ex. aluminium shows higher wear rate than stainless steel but significantly lower friction than stainless steel. The static co-efficient of friction values for stainless and ceramics deposited on unpolished steel are nearly the same; however, a wide difference can be noticed between them in the wear properties. The static co-efficient of friction values for ceramics deposited on polished steel are higher than the friction values of stainless steel but the wear resistance of the former is better than the latter. Friction in real materials is very difficult to predict because of the influence of wide range of variables on the measured friction values and hence, the friction values of materials always cannot correspond to their wear resistance. This method is particularly selected since there is a possibility that high-friction materials could give rise to troubles when they come into contact with a steel scraper, a metal utensil normally employed to remove loose deposits from the frying surface before the cleaning process, used in industrial frying bands and food processing equipments. However, the friction in real materials is very difficult to predict because of the wide range of variables and hence these values should be taken as indicative only, actual values will vary with temperature, lubricating material, atmosphere, etc., during the specific application.

CHAPTER 4

WORKING PRINCIPLES AND VALIDATION OF THE FRYING RIG

4.1. Frying rig

The frying rig is a specially designed, box-shaped construction made in our department workshop. The primary aim of the construction is to establish controlled conditions for fouling of different coatings on steel and aluminium plates (called frying discs) under realistic frying conditions. The rig allows control of heat fluxes and exact measurements of the crucial physical properties (temperature distribution and mass loss through evaporation) of real food products fried under realistic conditions. The principal components of the frying rig are shown in Figure 4.1. The heating surface of the frying rig is made up of an aluminium slab (300 x 300 x 25 mm) which rests on a thermostated hot-plate (300 x 300 mm) with a capacity of 3 kW (for complete description and working of the frying rig, see section 2.1 in paper I). An aluminium material was chosen for the purpose since the large mass and high conductivity of the aluminium slab is expected to provide adequate transfer of heat between the plate and the slab, also during the transient conditions arising when a cold product is placed on the frying disc. The whole frying rig is placed on a balance (35 kg max load, accuracy = ± 0.1 g) in order to continuously import the mass loss data into a computer.

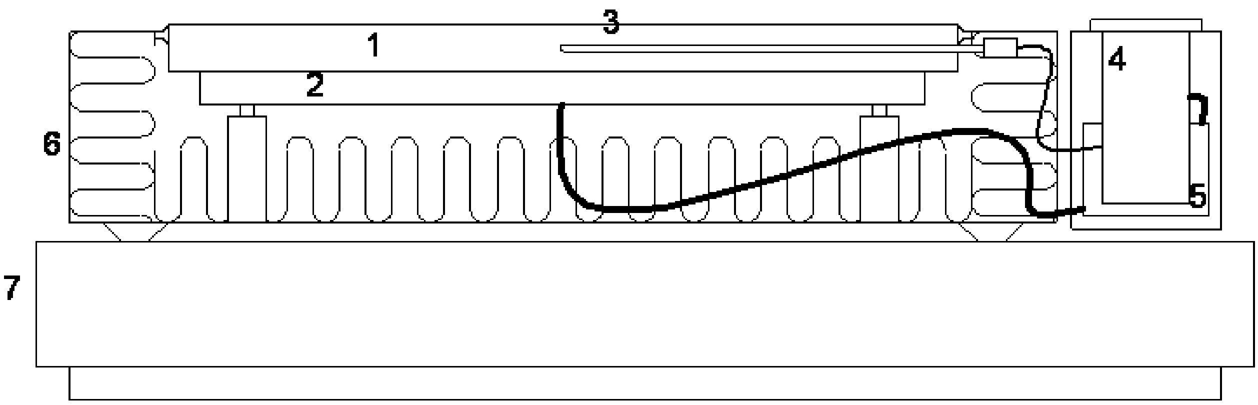


Figure 4.1. Principal components in the frying table: 1. Aluminium Plate 2. Heating Plate 3. PT100 sensor 4. Temperature Display 5. Relay 6. Insulated box 7. Balance Plate

Figure 4.2. Schematic view of the frying table resting on a balance

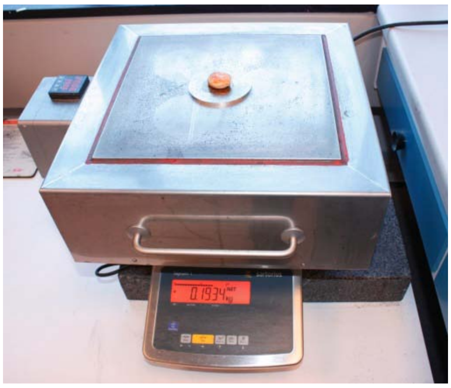


Figure 4.3. Photograph of the frying table showing the frying disc along with a piece of fried meat

4.2. Validation of the frying rig

The frying rig was validated by performing surface temperature and mass loss measurements which were described in detail in paper I. The reported results and the discussion in the upcoming sections were therefore mainly extracted from paper I.

4.2.1. Surface temperature measurements

In order to validate the surface temperature distribution of the frying rig, it was set to 200^{o}C and allowed to stabilize for 30 minutes; the surface temperature of the aluminium slab was then measured using a contact thermometer at 16 x 16 points regularly positioned in a rectangular array on the surface of the aluminium slab. The innermost 12 x 12 points defined the central area, and the remaining outer area of 2 point's width on all four sides defined the rim of the slab. The low standard deviation on the measurements (refer to section 3.1 in paper I) in the central area demonstrated that the heat flux was highly uniform. A statistical significant difference found between the average surface temperatures of the central area and the rim (refer to section 3.1 in paper I) shows that convective influx of cold air plays a noticeable, but negligible effect on the heat flux outside the central area. The surface temperature varied slightly from the set temperature (1-2^{o}C) due to differences in the convective heat loss from day-to-day variations in the environment. When an aluminium frying disc was placed on the slab and allowed to equilibrate for 10 minutes it was observed that the slab temperature in the vicinity of the disc increased slightly (about 2^{o}C) due to the local lowering of the heat flux (the disc has a little insulating effect). The surface temperature of the frying disc is less than the set temperature (Table 4.1); when pancake dough comes into contact with the frying disc, the interfacial temperature between the pancake and the frying disc changes a lot as can be seen in the temperature profiles measured during pancake baking (refer to Figure 3 and section 4.1 in paper IV).

4.2.2. Mass loss measurements

The validation of the mass loss measurements was made by frying pancakes on different surfaces at different temperatures. The frying discs were circular plates, cut by water-jet cutting, in stainless steel or aluminium, with a diameter of 90 mm and a thickness of 5 mm. To ensure good thermal contact, heat-resistant copper paste was applied to the bottom of the frying disc using a paint brush before the disc was placed on the frying rig. To test the effect of applying copper paste to the bottom side of the frying discs, a series of experiments with aluminium plates (ten with copper paste and ten without) were carried out at 160^{o}C and 200^{o}C, respectively, and the surface temperatures were recorded; the results are shown in Table 4.1. The statistical significant rise in the surface temperature of the frying discs when using copper paste demonstrates that the copper paste enhanced the thermal contact between the disc and the frying rig. However, the data also indicate that even when not using copper paste, the variation in surface temperature is small, and the thermal resistance between the discs and the slab is low.

Table 4.1. Temperature measurements on ten different aluminium surfaces with and without the use of copper paste at 160°C and 200°C

Set temperature (°C)	Use of copper paste	Mean surface temperature (°C)	SD[a] (°C)	t-value calculated
160	Yes	154.2	0.09	9.79 (P<0.001)
	No	152.0	0.20	
200	Yes	192.6	0.08	4.15 (P<0.001)
	No	191.2	0.32	

a - Standard Deviation

A pancake batter of suitable viscosity was developed from trial and error experiments (see section 2.2 in paper I). The pancake was fried for 600 seconds on one side; the procedure for frying is described in section 2.3 in paper I. Mass loss because of evaporation was monitored continuously by recording the weight every second; the mass was found to decrease approximately linearly in the range of 100 to 500 s. After frying, the pancake was removed from the surface using a metal spatula. For each type of coating, frying experiments were carried out at three different set temperatures, 160, 200 and 240°C, with five repetitions for each temperature. After cleaning, the frying discs were re-used for the next experiment.

Table 4.2 - Mean values of mass loss from pancake baking experiments

Temperature / Material	Mean mass difference in g over 100 – 500 s		
	160 °C	200 °C	240 °C
Teflon (Al Mg 5754)[a]	0.94	1.34	1.67
Aluminium Al Mg 5754	1.16	1.38	1.62
316 Stainless Steel	0.81	1.51	1.85
TiAlN (UP 316 SS)[b]	1.05	1.22	1.69
TiAlN (EP 316 SS)[c]	1.02	1.30	1.86
ZrN (UP 316 SS)[d]	0.79	1.33	1.50
ZrN (EP 316 SS)[e]	0.99	1.31	1.77
ZrO_2 (UP 316 SS)[f]	1.08	1.28	1.90
ZrO_2 (EP 316 SS)[g]	1.14	1.31	1.79

Standard deviation on the means (five repetitions) : 0.11 g

The pancake mass difference measurements on various surfaces at two different temperatures are shown in Table 4.2. An ANOVA shows that there is no significant difference in the mass loss profile for tests using different plates at the same temperature ($F = 1.50$; d. f. = 8, 68; $P > 0.05$) and also that different thermal conductivities of the plates (e.g. aluminium versus stainless steel) do not play a significant role for the rate of evaporation, which means that the heat and mass transfer from the frying surface to the pancake and the rate of evaporation is determined by the pancake itself. This is a reasonable conclusion since pancake dough is viscous and soon solidifies, causing the water transport to the surface to be controlled by diffusion. As long as evaporation takes place, the temperature at the upper surface of the pancake must be around 100 ^{o} C or less. The temperature produced a profound effect on the rate of the evaporation ($F = 32.5$; d. f. = 1, 68; $P < 0.001$) by creating a steeper temperature gradient from the bottom to the top of the pancake (see section 4.1 in paper IV).

4.3. Advantages of the frying rig

The validation of the frying rig by surface temperature and mass loss measurements shows that the heat flux is uniform over the entire central area of the aluminium slab which constitutes the hot surface of the rig, and that the baking process itself is also reproducible when using the frying rig. The effect on surface temperature arising from local disturbances and day-to-day variations in the heat flux are small and negligible when comparing with the span of relevant set temperatures (in this case 160, 200 and 240^{o}C). Furthermore, the frying rig can be used for quantitative studies of heat and mass transfer during contact baking of pancake (paper IV). The frying rig presented and validated here thus has a wider possibility of use as an experimental set-up in food engineering.

The frying rig has been constructed in a way that allows a ready change of both the substrate and the surface material of the frying surface, and the tests can be done on small specimens (frying discs of 90 × 5 mm) coated with different materials in order to investigate the influence of different surface material properties; the evaluation of the non-stick properties became more feasible when using the frying rig. The testing of the non-stick properties of different surfaces in the oven and on the frying rig (see section 3.4 in paper I) evidently demonstrated that it is not realistic to test non-stick properties of contact frying processes in a convective oven, since the test performed in a convection oven simply reflects non-stick properties in a convective oven and cannot be extrapolated to contact frying, where the mechanism of heat and mass transfer in the food is different. This demonstrates that the frying rig has a number of unique benefits for testing different surfaces for their non-stick properties in contact frying processes.

CHAPTER 5

METHODS FOR EVALUATING THE NON-STICK PROPERTIES OF DIFFERENT SURFACES

5.1. Adhesion and Cohesion

Adhesion which is defined as the sticking together of two materials (Kilcast and Roberts, 1997; Michalski et al. 1997; Nelson, 1995) is an important issue in the food industry (Michalski et al. 1997). The force required to separate the two adhering materials is termed as the force of adhesion (Hoseney and Smewing, 1999). Although the definition sounds simple, adhesion phenomenon is rather complex and difficult to measure in many cases (Kilcast and Roberts, 1997; Nelson, 1995). In the case of hindering fouling or removing a food material already deposited on the surface of process equipment, there are two types of forces to be considered: (i) cohesive (ii) adhesive. Cohesive force exists between the molecules of the deposit whereas the adhesive force exists between the deposit and the surface. Since the removal of deposit from the surface can occur as a result of adhesive or cohesive failure or a combination of both (Liu et al. 2006), it is often obligatory to observe whether the failure is adhesive or cohesive in nature. If no residues are left on the surface, there occurred a failure of the bond between the deposit and the surface and hence the failure is named as adhesive (Dobraszczyk, 1996; Hoseney and Smewing, 1999; Kilcast and Roberts, 1997). The failure is termed as cohesive if the adhesive force is higher than the cohesive force and residues were therefore found to remain on the surface (Dobraszczyk, 1996; Kilcast and Roberts, 1997; Michalski, 1997).

5.2. Adhesion theories

The phenomenon of adhesion involves several fields such as mechanics, thermodynamics and chemistry (Michalski, 1997). Hence, numerous mechanisms are proposed for adhesion between an adhesive (in this case, food deposit) and the adherend (in this case, frying surface) (Allen 1987; Allen 1993; Michalski 1997; Mittal 1977; Nelson 1995):

(i) mechanical interlocking

(ii) wetting

(iii) chemical adhesion

(iv) electrostatic forces

Mechanical interlocking

Adhering of two materials can occur as a result of locking through their pores and asperities which is termed as mechanical interlocking; the oldest and most widely accepted theory for adhesion (Michalski, 1997). In case of adhesion between coating and substrate, substrate roughness is expected to offer a mechanical interlocking for keeping the coating in place. Likewise, in case of adhesion between the food deposit and the frying surface, roughness of the frying surface plays a vital role in entrapping impurities or bacteria (Hilbert, 2003; Whitehead, 2006) within the grooves by mechanical interlocking process. Hence, visualization and measurement of surface roughness and topography is often necessary to understand the role of mechanical interlocking in adhesion studies (Michalski, 1997).

Wetting

Wetting is an important theory in explaining the adhesion phenomena between a liquid and a solid. This theory suggests that if a liquid wets and spreads completely on a surface, there is sufficient interaction between their molecules at the interface of the liquid and the solid where weak bonding forces such as van der Waals forces, particularly the London dispersive forces become effective, resulting in good adhesion (Mittal, 1977; Nelson, 1995). London dispersion forces, named after the German-American physicist Fritz London, are weak intermolecular forces that arise from the interactive forces between instantaneous multipoles in molecules without permanent multipole moments. This theory could play a significant role in determining the adhesion if the food products are liquid or semi-solid in nature (Michalski, 1997).

Chemical adhesion

When the two adhering materials undergo chemical reaction, primary valence bonds or covalent bonds can be formed resulting in chemical adhesion (Mittal, 1977); the bond strength in such cases is greater than the van der Waals forces (Nelson, 1995). This theory is more relevant when there is enough contact time of contact between the two adhering materials (Michalski, 1997).

Electrostatic forces

This theory suggests that an electrical double layer could be formed if a charge transfer takes place between the two adhering materials; the adhesive and the adherend can be considered as a capacitor in which the intimate contact at their interface could result in attractive forces. This theory was considered responsible for adhesion between proteins and surfaces, in particular stainless steel (Michalski, 1997).

5.3. Adhesion measurement techniques

5.3.1. Adhesion measurement with texture analyzer

Texture analyzer is widely used for adhesion studies in food industries (Dobraszczyk, 1996; Hoseney and Smewing, 1999; Kilcast and Roberts, 1997). We have therefore developed a method using texture analyzer with an aim to measure the force of adhesion between a fried pancake and the frying surface; the experiments were carried out using aluminium and PTFE (coated on UP 316 SS) surfaces.

The procedure for pancake frying experiments was described in section 2.3 in paper I; a 50 g pancake was used here and a removable stainless steel ring was made to fit to the frying disc during pancake frying experiments. In order to avoid the sticking of pancake to the stainless steel ring, the ring was sprayed with vegetable oil which is normally sprayed on baking trays to avoid adhesion between the bread and the tray during bread baking process. The higher thermal expansion of aluminium as compared to stainless steel makes the aluminum plate to expand when it is heated; thus, making the aluminium plate to fit tightly to the stainless steel ring during frying experiments. The pancake dough was poured onto the hot surface and a porous stainless steel holder (shown in Figure 5.1) was then pressed into the pancake dough. The pancake was fried for 600 seconds on one side. After pancake frying, the stainless steel ring was removed from the frying disc. The frying disc along with the fried pancake and the steel holder was fixed on the testing platform; the steel holder was fitted to the probe of the texture analyzer. During the measurement, the steel holder was pulled in tension where the probe causes the pancake along with the steel holder to separate from the disc. A porous holder was chosen for the purpose because the pancake can adhere better to a porous holder than to a simple flat holder during pancake frying; thus, avoiding the breakage between the pancake and the holder during testing. The force versus distance curve was generated by the texture analyzer where the peak force was considered as a measure of stickiness. Aluminium and PTFE (coated on UP 316 SS) discs were tested using this method; three trials were performed for each disc following frying at 160^{o}C and the results are summarized in Table 5.1.

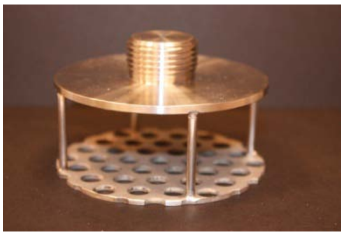


Figure 5.1. Stainless steel holder used for adhesion measurement with texture analyzer

Table 5.1. Peak force measured for two different surfaces using texture analyzer method

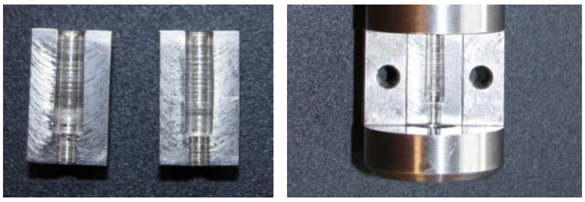
Surface Material	Peak Force (N)		
	Trial I	Trial II	Trial III
Aluminium (Al Mg 5754)	8.0	27.5	38.0
PTFE	37.0	49.3	67.9

The results obtained for both the surfaces as shown in Table 5.1indicate that a large deviation exists between one measurement and the other which means that the experiments were not reproducible. Moreover, the peak forces obtained for PTFE were higher than the peak forces for aluminium which is quite contradictory; the mode of failure in both cases is adhesive at the interface between the pancake and the frying surface. The reason for the huge standard deviation between the measurements could be caused by the tendency of the pancake to stick to the steel holder during frying which could hinder its ability to stick to the frying surface. Since the results cannot be replicated, further experiments for testing other surfaces were not carried out using this method.

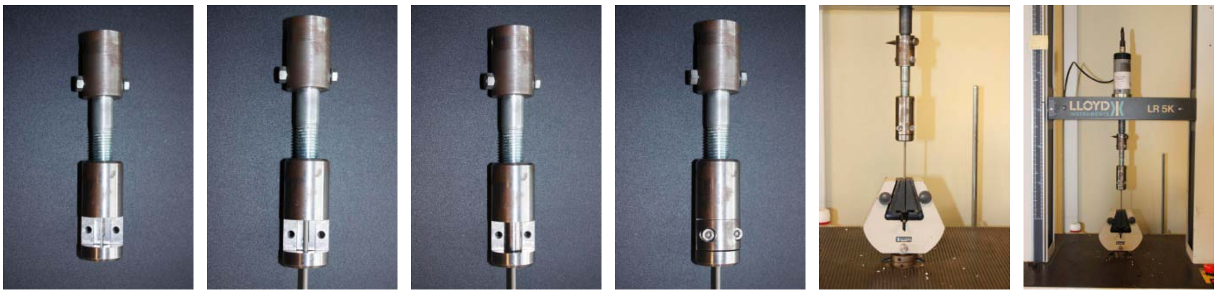
5.3.2. Adhesion measurement with a special experimental set-up

The adhesion of coated steel wires is typically tested at Accoat A/S by measuring the force of adhesion between the coating and the steel cable by means of an experimental set-up, specially designed at Accoat A/S (Figure 5.2f); the steel set-up was therefore employed to measure the force of adhesion between the pancake and the stainless steel cable.

In this method, a stainless steel wire which is 2 mm thick and 10 cm long was dipped into the pancake dough (for composition, refer to section 2.2 in paper I) using a dip-coater at a speed of 36.5 cm/min until 2 cm of the cable was completely coated with the pancake dough. The cable was then withdrawn from the dough and heated in a household convection-oven (Lytzen, Herlev, Denmark) at the required temperature: 160 or 200°C for 10 minutes. The design involves a special cable holder which consists of two parts as shown in Figure 5.2a. In the first step, one part of the cable holder was fitted into the steel set-up as shown in Figure 5.2b&c. Subsequently, one end of the stainless steel cable which was coated with the pancake was inserted into the cable holder similar to figure 5.2d (stainless steel wire with adhered pancake was not shown in the figure). The other part of the cable holder was then placed on top of the stainless steel cable as shown in figure 5.2e and screwed properly as shown in figure 5.2f. The experimental set-up along with the stainless steel cable was then fitted to the material testing instrument as shown in figure 5.2g. The steel set-up was pulled in tension at a speed of 150mm/min, with the stainless steel cable clamped at the other end while the cable holder causing the pancake to separate from the cable; the force versus distance curve was generated by the material testing instrument where the peak force was considered as a measure of stickiness. A stainless steel cable and a PTFE coated stainless steel cable was tested using this set-up where the experiments were carried out at three different baking temperatures 160, 200 and 240°C with five repetitions for each temperature. The results are summarized in Table 5.2.



(a) (b)



(c) (d) (e) (f) (g) (h)

Figure 5.2. Experimental set-up used in adhesion measurement with stainless steel cable (a) cable holder in two parts (b) one part of the cable holder placed in the experimental set-up (c) distance view of the steel set-up with one part of the cable holder (d) stainless steel cable inserted into the cable holder (e) other one part of the cable holder placed on top of the stainless steel cable (f)

stainless steel cable fitted into the experimental set-up by means of two screws (g) experimental set-up fitted into the testing instrument and other end of the stainless steel cable fixed at the bottom by means of a clamper (h) distance view of the testing instrument with the experimental set-up.

Table 5.2. Mean values of peak force at different temperatures

Material	Temperature (^{o}C)	Mean Peak Force in Newton (five repetitions)
PTFE	160	16.1
	200	19.1
	240	28.1
Stainless steel	160	107.9
	200	116.0
	240	124.8

Standard deviation on the means of peak force (five repetitions): 0.72 Newton

The surface material ($F = 2.6 \times 10^4$; d. f. = 1, 20; $P < 0.001$) and temperature ($F = 207$; d. f. = 2, 20; $P < 0.001$) produced a significant effect on the peak force values. The force required to remove the pancake adhering to PTFE coated stainless steel cable was much lesser than the force required to remove the pancake adhering to stainless steel cable which indicates the better performance of PTFE compared to stainless steel. These results show that the method is able to distinguish between different materials; however, the mode of failure observed in these experiments was mainly cohesive in nature since the pancake adhered to the cable cannot be removed completely instead it was removed in small chunks leaving deposits on the cable. This could possibly end up in measuring the cohesive force within the pancake instead of measuring the adhesive force between the pancake and the cable. Moreover, the force required to remove the pancake from a flat frying surface would probably be different from the force required to remove the pancake from a cable. We therefore developed a method to measure the force of adhesion between the pancake and a flat frying surface in which it is possible to remove the fried pancake directly from a flat frying surface by means of a steel scraper which is described in detail in the following section.

5.3.3. Subjective evaluation of adhesiveness

Adhesiveness or stickiness measurements within the food industry are often based on visual inspection and subjective assessment (Dobraszczyk, 1996). Human assessments of non-stick properties are acknowledged and commonly applied in food science and technology (Dhaliwal & Macritchie, 1990; Fenn et al. 1994). Standardized subjective techniques for evaluating the non-stick and easy clean properties were developed and followed in coating industries like Whitford for testing the newly coated frying pans (Whitford test method 199A & 199B). Furthermore in the literatures (Haering 2000; Faulkner 2001; Groll 2002; Hayakawa 2007), subjective assessment using a descriptive scale for giving grades is used to evaluate the adhesion of the food to the frying surface. A subjective evaluation of the non-stick properties of different test coatings was therefore chosen as a valid and reliable approach in the present work.

The pancake frying experiments were performed on different surface materials using the frying rig (for procedure, refer to section 2.3 in paper I). In this case, a 10 g pancake was used for the frying experiments instead of a 50 g pancake since: (i) use of steel ring can be avoided during pancake frying experiments (ii) it was much easier to use a small pancake for subjective evaluation purposes. However, the experimental procedure developed using a 50 g pancake was extrapolated for quantitative studies of the heat and mass transfer in contact baking processes (refer to paper IV). After frying, the pancake was removed from the frying surface using a metal spatula and the ease with which the fried pancake can be removed from the frying disc was evaluated subjectively according to the procedure described in section 2.5 in paper I. The results are shown in Table 5.4.

The release ratings indicate that the surfaces with a rating of 1 has excellent non-stick properties and surfaces with a rating below 3 has good non-stick properties; the surfaces which grab the attention. The rating of 4 to 5 clearly illustrates the poor non-stick performance of the surfaces which are of no interest in this case.

Table 5.3. Release ratings for different surface materials after pancake frying at different temperatures

Surface	Set temperature (°C)	Release ratings (five repetitions) Frying rig Mean	Minimum	Maximum
Teflon® (Al Mg 5754)	160	1,0	1	1
	200	1,0	1	1
	240	1,0	1	1
Aluminium Al Mg 5754	160	2,4	2	4
	200	4,6	4	5
	240	4,0	4	4
316 Stainless Steel	160	2,0	2	2
	200	3,0	3	3
	240	3,0	3	3
TiAlN (UP 316 SS)	160	2,0	2	2
	200	3,0	3	3
	240	1,4	1	2
ZrN (UP 316 SS)	160	2,0	2	2
	200	3,0	3	3
	240	3,0	3	3
ZrO_2 (UP 316 SS)[f]	160	2,0	2	2
	200	3,0	3	3
	240	3,0	3	3
TiAlN (EP 316 SS)	160	4,6	3	5
	200	4,6	4	5
	240	3,2	3	4
ZrN (EP 316 SS)	160	5,0	5	5
	200	4,0	4	4
	240	5,0	5	5
ZrO_2 (EP 316 SS)	160	5,0	5	5
	200	4,0	4	4
	240	5,0	5	5

Standard deviaition on the means of ratings (five repetitions) - 0.15

The results shown in Table 5.3 reveal the good non-stick properties of PTFE since it obtained a rating of one in all experiments. The release ratings indicate that a clear difference can be noticed between the performance of stainless steel and aluminium at high temperatures: 200 and 240°C; there is no such difference at 160°C. This is in accordance with Kaushik and Bala (2010) who stated that stainless steel is non-reactive and easy-to-clean when compared to that of aluminium. The results also demonstrate that the non-stick performance of different ceramics deposited on unpolished steel does not seem to be superior to that of stainless steel except TiAlN which shows better performance at 240^{o}C. When we observe the release ratings for different ceramic materials (both deposited on unpolished and polished steel), it is apparent that the difference in ceramic material composition i.e., TiAlN, ZrN or ZrO_2 does not produce a significant difference in their non-stick performance at 160 and 200^{o}C. However, TiAlN demonstrates a better performance than ZrN or ZrO_2 at 240^{o}C. An explanation for this could be that these ceramic nitrides and the stainless steel oxidize when they come into contact with air (Faulkner, 2001), and these protective oxide layers are likely to behave similar in their sticking behaviour with pancake at 160 and 200^{o}C.

Release ratings for different surfaces on the frying rig and in the oven

The pancake frying experiments were performed on different surface materials on the frying rig (for procedure refer to section 2.3 in paper I) as well as in a household convection-oven (for procedure refer to section 2.6 in paper I); after frying, the pancake was removed from the frying surface using a metal spatula and the non-stick properties of the different surfaces were evaluated as described in section 2.5 in paper I.

PTFE obtained a rating of one in all cases, both on the frying rig and in the oven as shown in Table 5.3. The release rating is five for all surfaces (except PTFE) at all temperatures when tested in the oven; however, the performance of the same surfaces varied to a great extent when testing on the frying rig (Table 5.3). This indicates that the frying rig offers more realistic test conditions for discriminating between different surfaces than the convection oven; there is, certainly, a distinct difference exists between the heating mechanism that takes place in an oven and the frying table.

5.3.4. Adhesion measurement with steel scraper

In order to exactly measure the force of adhesion, it is essential to have a method where a clean separation is possible at the interface between the deposit and the surface (Hoseney and Smewing, 1999); a direct measurement of the force of adhesion between the pancake and the frying surface was made feasible by utilizing the present method where a steel scraper was employed to remove the entire pancake at the interface from different frying surfaces.

In order to replicate the pancake scraping practice, a rectangular steel scraper was particularly chosen which is analogous to the dough scrapers used in the food industry. A schematic view of the test apparatus is shown in Figure 5.3. A detailed description about the apparatus and testing procedure is described in section 2.7 in Paper I. The force of adhesion measurements, in this case, was carried out with a 2g pancake.

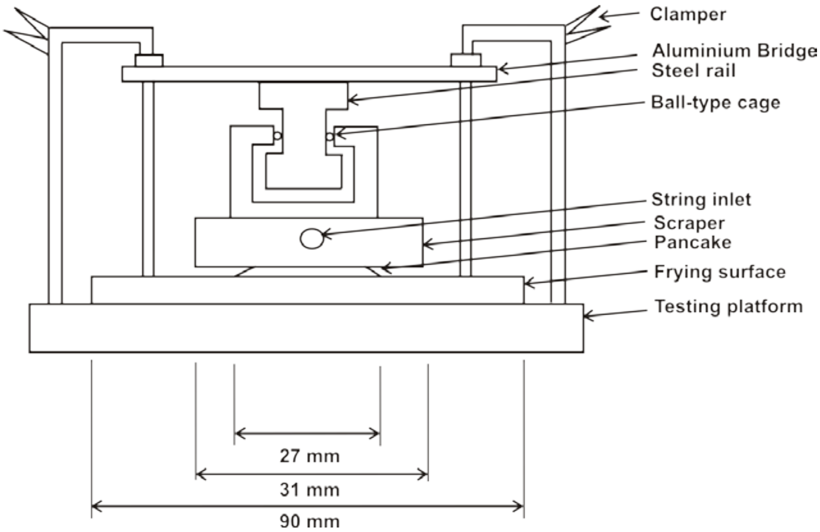


Figure 5.3. Schematic view of the adhesion measurement set-up with steel scraper

Table 5.4. Mean values of peak force measured using steel scraper at different temperatures

Surface Material	Mean peak force in Newton (three repetitions)	
	$160^{o}C$	$200^{o}C$
Teflon (Al Mg 5754)	0.0	0.0
Aluminium Al Mg 5754	2.4	6.1
316 Stainless Steel	1.9	4.3
TiAlN (UP 316 SS)	1.5	3.3
ZrN (UP 316 SS)	1.7	4.4
ZrO_2 (UP 316 SS)	2.4	5.5
TiAlN (EP 316 SS)	6.9	9.2
ZrN (EP 316 SS)	6.2	9.7
ZrO_2 (EP 316 SS)	7.2	9.6

Standard deviation on the means of peak force (three repetitions) : 0.42 Newton

The factors such as surface material, temperature and surface topography produced a significant effect on the peak force values (for details, refer to section 3.6 & 3.7 in paper I). Our results show that the performance of ceramics (deposited on unpolished steel) was not superior to stainless steel. As expected, the peak force values significantly increased with increase in temperature. It was identified that the surface topography played a crucial role in the performance of different surfaces where ceramics deposited on unpolished steel performed better than the ceramics deposited on polished steel. The peak force values obtained for different surfaces at two different temperatures are shown in Table 5.4.

5.4. Correlation between subjective and objective method

The release ratings obtained using subjective evaluation procedure is shown in Table 5.5 and the peak force values measured using steel scraper is shown in Table 5.4. The release ratings and the peak force values at two different temperatures, 160 and 200^{o}C, are plotted against each other in figure 5.4, where a good correlation (R^2=0.92) was obtained between them (for detailed explanation about the figure, refer to section 3.5 in paper I). This means that the method developed to measure the force of adhesion was able to reflect the practice oriented method, normally used to remove the fried food from the frying surface. The objective method was capable of distinguishing different surfaces according to their non-stick abilities as well as the subjective evaluation method was equally effective for screening different surfaces.

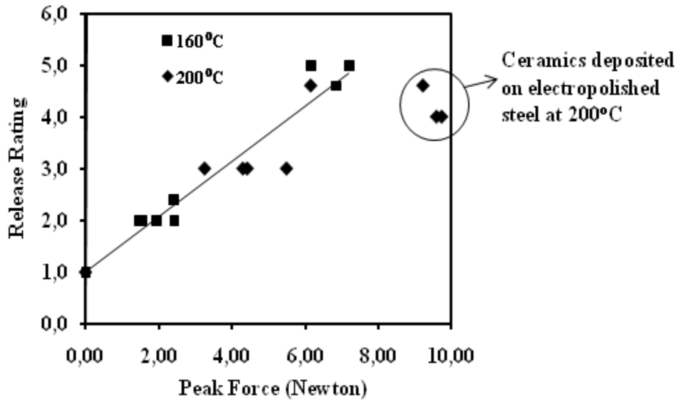


Figure 5.4. Plot of peak force (in Newton) versus release rating

5.5. Pancake as a food model for testing the non-stick properties

In the evaluation of non-stick properties of different surface materials, we have chosen pancake as a food model in accordance with the industry practice. The results from subjective evaluation and force of adhesion measurements indicate that the pancake has proven to be a good model for discriminating between the non-stick performances of different frying surfaces. The investigation of non-stick properties becomes difficult if the food does not stick to the frying surface; the ability of the pancake to stick to the frying surface made it feasible to evaluate the non-stick properties of different frying surfaces.

5.6. Conclusion

The intial experiments to evaluate the non-stick properties of different surfaces were carried out using a 50 g pancake. In those experiments, texture analyzer was used to measure the force to pull the pancake from the frying surface. Since the method did not give reproducible results, further test methods have been developed. In one of the other test methods, where a special experimental set-up was used to measure the adhesiveness between the pancake and the cable, cohesive failures were observed between the pancake and the cable. Hence, it was decided to carry out subjective evaluation procedures to test the non-stick properties of different surfaces by using a 10 g pancake instead of a 50g pancake. The subjective evaluation procedure was found to be less time-consuming and rather easy to reproduce. It is an appropriate procedure for screening different surfaces since a good non-stick surface is apparently characterized by ratings which are below 3 and the rating was reproducible with a low standard deviation (around 0.3 units on a 1-5 integer scale). Subsequently, a method employing steel scraper was used to measure the force of adhesion between the pancake and the frying surface. The peak force values measured as the force of adhesion between the pancake and different surfaces using the steel scraper was able to discriminate between the non-stick properties of different surfaces. The release ratings obtained by the subjective method were found to be in good agreement with the peak force values measured by the objective method. The methods developed and tested for analyzing the non-stick properties of surfaces are well-suitable for screening different surfaces in industries.

CHAPTER 6

CLEANING PROPERTIES OF DIFFERENT SURFACES

6.1. Fouling

Fouling is defined as “the unwanted build-up of deposits on a surface” (Fryer and Christian, 2005). Fouling is a complex phenomenon which affects the costs and processes in many industries (Balasubramaniam and Puri, 2010; Kukulka, 2010); fouling in the food industry is more critical than in other industries (Changani et al. 1997). A major concern in the food industry is to deal with the problems of fouling and the cleaning of surfaces in contact with foods (Bird and Fryer, 1991). Adhesion of material to the surface and cohesion between elements of the material result in fouling deposits (Liu et al., 2002). A variety of different causes can result in fouling, and the sequence of processes that are fundamental for deposit formation is complex and diverse (Changani et al. 1997).

A profound knowledge of the relation between the fouling material and the fouled surface is of utmost importance in the attempt to reduce the amount of fouling in the food industry (Forster and Bohnet 1999). Roughly, fouling is affected by a combination of chemical and physical factors: (i) Chemical effects occur as a result of thermally induced reactions of the three main food constituents: carbohydrates, proteins and fats. (ii) Physical effects typically arise from the physico-chemistry and topography of the frying surface in contact with the food.

To reduce the fouling problem in heat transfer equipment, many studies have been carried out to analyze the influence of different surface materials on the fouling on heat-exchangers (Balasubramanian and Puri, 2009; Gordon et al. 1968; Rosmaninho et al. 2007; Muller-Steinhagen and Zhao, 1997; Yoon and Lund, 1994). Balasubramanian and Puri (2009) studied the effect of Ni-P-PTFE and lectrofluor (fluoropolymer based coating) on the reduction of milk fouling and reported that the lectrofluor coating reduced fouling to a larger extent than the Ni-P-PTFE coating. The studies by Gordon et al. (1968) shows that the PTFE - coated pipe gave higher recovery of milk deposits than the stainless steel pipes. Rosmaninho et al. 2007 analyzed the effect of different surface modifications on the reduction of dairy fouling and found out that the Ni-P-PTFE coating was the most promising one. Muller-Steinhagen and Zhao (1997) investigated different surface alloys made by ion implantation technology on the reduction of $CaSO_4$ scale formation and concluded that the stainless steel surface implanted with silicon fluoride ion significantly reduced the scale formation. Even though PTFE is commonly used in many industries for reducing fouling, there are also studies indicating the poor performance of PTFE. Yoon and Lund (1994) analyzed the effect of different surface treatments on the reduction of milk fouling and concluded that there was no significant reduction of cleaning time on the PTFE-coated plate.

A few studies were carried out to evaluate the effect of surface treatment on the cleaning of model food soils (Saikhwan et al. 2006; Mauermann et al. 2009). Saikhwan et al. (2006) studied the effect of different surface modifications on the removal of baked tomato paste using fluid dynamic gauging and reported that the Ni-P-PTFE surface showed lower adhesion with the tomato paste. Mauermann et al. (2009) studied the influence of different surface modifications on the cleaning of potato starch and whey protein solutions and concluded that the starch deposits on Fluorinated Ethylene Propylene (FEP) modified surfaces were reduced by up to 76% and the protein deposits on nanocomposite modified surfaces (inorganic and hybrid coatings) were reduced by up to 34% in contrast to stainless steel.

To the best of our knowledge, there is a lack of systematic studes of the effect of different surfaces in reducing the fouling resulting from contact frying of foods. Since the composition of diffrent foods varies, the deposits resulting from thermally induced reactions in each food will vary depending on their composition. Frying one single type of food on a particular surface will therefore not be sufficient to recognize the efficiency of the surface in minimizing fouling. Moreover, oil is often used as a frying media for contact frying purposes (Soupas et al. 2007). Therefore, in the present work, the cleaning properties of different surfaces were analyzed by frying three different kinds of foods (carrot, sweet potato, turkey meat) with and without the use of oil; the frying experiments were carried out under controlled conditions using the frying rig. The results obtained in this work were already presented at the conference, Fouling and Cleaning in Food Processing, Cambridge, UK; the results were published in the conference proceedings (Paper III).

Raw Materials

The foods were carefully chosen based on their composition and how they represented the three main constituents of food: proteins, carbohydrates and lipids. Turkey meat was chosen for its high protein content, carrot for its reducing sugar (glucose) content and sweet potato for its starch content; vegetable oil (rapeseed oil) was chosen to represent fats. The foods were purchased from Netto, a Danish supermarket. The sweet potato and carrot were cut into rectangular pieces of about 5.0 x 2.0 cm with a thickness of about 0.2 - 0.3 cm (the value is misprinted in paper III). The fresh meat was cut into approximately 1 - 1.5 cm thick flat pieces and frozen for an hour to be able to cut the meat in a proper shape; the meat was then cut into round pieces which were about 4.0 cm in diameter and 1.5 cm in thickness. The composition of the foods shown in Table 6.1 was taken from the Danish Food Composition Databank - www.foodcomp.dk.

Table 6.1. Constituents of Foods

Food	Water	Carbohydrates					Protein	Fat	Ash
		Sugar			Starch	Dietary fibre			
		Fructose	Glucose	Saccharose					
Carrot	89.9	1.9	2.5	1.6	0.0	2.9	0.7	0.4	0.7
Sweet Potato	80.3	0.8	0.9	2.5	10.1	2.7	1.3	0.3	1.1
Turkey Meat	75.5	0.0	0.0	0.0	0.0	0.0	21.9	2.2	1.0
Rapeseed Oil	0.0	0.0	0.0	0.0	0.0	0.0	0.0	100	0.0

Frying experiments

The frying experiments were carried out on different surface materials, specified in Table 6.3 (for a detailed procedure of the frying experiments, refer to section 2.2 in paper III). After each experiment the fouled frying disc was removed from the frying table, cleaned and rated according to the procedure mentioned in the following section. For each type of surface material, the frying experiments were carried out with different foods with and without the use of oil at two different temperatures: 200 and 240^{o}C.

6.2. Cleaning

Plett, 1985 defines cleaning as “a heterogeneous chemical reaction involving six major mechanisms: bulk reaction of detergents; transport of detergents to the soiled surface; transport into the fouled layer; cleaning reaction (including physical and physicochemical transformations, and chemical reactions); transport of cleaning reaction products to the interface; transport of products to the bulk solution”. The ultimate aim of cleaning is to attain a hygienic surface that is free of any dirt, micro-organisms or food deposits. The cleaning agent chosen is based on the nature and structure of the deposits to be removed as shown in Table 6.2 (Plett, 1985):

Table 6.2. Typical components in food process fouled layers and their solubility (Plett, 1985)

Component	**Solubility**	**Removal**	**Heat Alterations**
Sugar	Water : Soluble	Easy	Caramelization
Fat	Water : Insoluble Alkali : Poor Acid : Poor	Difficult (Good with surfactants)	Polymerization
Protein	Water : Poor Alkali : Good Acid : Medium	Difficult Good Difficult	Denaturation
Mineral salts monovalent	Water : Soluble Acid : Soluble	Easy	Precipitation
Mineral salts polyvalent	Water : Insoluble Acid : Soluble	Difficult	

Cleaning treatment in the food industry

In the food industry, two types of cleaning treatments are regularly employed (Bird and Fryer, 1991):

(i) Two stage

In a two stage cleaning process, both alkali and acid are employed for cleaning. In the first step, a suitable alkali such as sodium hydroxide is used for cleaning purposes followed by rinsing with acid, nitric or phosphoric acid. However, this process requires several rinsing steps with water in order to remove the excess acid left on the cleaning surface.

(ii) Single stage

In a single stage process, formulated detergents are mainly used. These types of detergents usually contain certain compounds such as surfactants or chelating agents; the added surfactants will enhance the wetting and foaming properties of the detergents thereby assisting in the cleaning process. The single stage process is widely used in the food industry because surfaces can be cleaned in a shorter time compared to the two stage process (Changani et al.1997).

Cleaning treatment for open food process equipments

Manual cleaning is often employed in the cleaning of open food process equipments where the visible deposits are removed by brushing, scraping, scrubbing or rinsing with low pressure water (Lewan, 2003; Salo, 2006). A combination of chemical (single stage process) and mechanical (scrubbing action) cleaning (Wirtanen et al. 1995) was therefore chosen for cleaning the fouled surfaces; the efficiency of cleaning can also be improved by a mechanical action (Boulané-Petermann, 1996).

6.3. Cleaning treatment after contact frying of different foods

The cleaning of open food process surfaces usually involves foam or gel cleaning (Salo, 2006). Foam cleaning was performed with the chosen cleaning solution: FOAM 235 (ITW Novadan ApS, Kolding, Denmark) is a clear, colourless liquid containing 15-30% potassium hydroxide, <5% ethanol, <5% alkylpolyglycosid, <5% non ionic surfactant and <5% amphoionic surfactant. The solution was diluted to 5% with water for all the cleaning experiments. Since the fouling deposits resulting from these types of frying experiments (section 6.3) could mainly involve sugar, fat and protein, an alkaline cleaning solution with added surfactants will solve the purpose. The steps followed in the cleaning procedure were similar to Wirtanen et al. (1995), the fouled frying disc was cleaned by

(1) rinsing with water for 1 minute

(2) soaking in the cleaning solution for 20 minutes and by final rinsing with water

(3) a household yellow cleaning sponge by moving it parallel to the surface without exerting any force and by final rinsing with water

(4) hard scrubbing using a household yellow cleaning sponge and by final rinsing with water

(5) a Scotchbrite® sponge since the stains are difficult to remove using a household cleaning sponge.

A cleaning rating, from a scale of 1 to 5, was assigned for the frying disc according to the following evaluation: rating 1 (if it became clean after step 1) to rating 5 (if it became clean after step 5); each frying disc was visually examined and photographed after every fouling, rinsing and cleaning step. Table 6.1 shows the cleaning ratings for different surfaces after frying three different foods with and without the use of oil at two different temperatures. The cleaning ratings are interpreted so that surfaces with a rating of 1 and 2 are easy to clean since they were totally clean by means of chemical treatment without the need for a mechanical action; those with a rating of 3-5 are difficult to clean since they were not entirely clean by use of chemical treatment alone and hence, an involvement of essential mechanical action is obligatory to achieve a complete clean surface.

Table 6.3. Cleaning ratings for different surfaces after frying three different foods with and without the use of oil at two different temperatures (the table is extracted from paper III)

Coating Material	Use of oil for frying	Cleaning ratings					
		Turkey Meat		Carrot		Sweet Potato	
		200 ^{0} C	240 ^{0} C	200 ^{0} C	240 ^{0} C	200 ^{0} C	240 ^{0} C
UP 316 SS	Yes	3.4	5.0	3.4	4.4	2.0	4.0
	No	2.4	3.0	2.6	4.2	1.2	2.0
TiAlN (UP 316 SS)	Yes	4.0	4.2	3.4	4.8	2.0	2.4
	No	2.0	2.2	2.4	2.8	1.0	1.8
TiAlN (EP 316 SS)	Yes	2.0	3.4	2.0	3.4	1.2	1.4
	No	2.0	1.8	1.6	2.4	1.0	1.4
ZrN (UP 316 SS)	Yes	2.2	3.2	2.6	4.4	1.4	3.6
	No	2.0	2.8	2.2	3.4	1.4	1.2
ZrN (EP 316 SS)	Yes	2.2	3.2	2.0	2.8	1.2	2.2
	No	1.8	2.2	2.0	2.0	1.0	1.2
ZrO_2 (UP 316 SS)	Yes	2.6	3.2	2.2	3.6	1.6	2.8
	No	2.0	2.4	2.0	3.8	1.4	1.4
ZrO_2 (EP 316 SS)	Yes	2.2	3.4	2.0	3.4	1.2	2.4
	No	2.0	2.0	1.8	2.6	1.0	1.0
QC (Al, Fe, Cr)	Yes	2.0	3.0	2.0	3.4	1.0	1.6
	No	1.2	1.4	1.6	2.0	1.0	1.2
Silicone	Yes	1.0	1.4	1.4	1.4	1.2	1.0
	No	1.2	1.6	2.0	3.0	1.4	1.0
PTFE	Yes	1.0	1.2	1.0	1.2	1.0	1.0
	No	1.0	1.0	1.2	1.6	1.0	1.0

6.4. Factors affecting the cleanability of different surfaces

In the following sections, the different factors: factors related to the frying surface in contact (surface material, surface treatment and surface roughness) and factors related to the frying process (food type, temperature, and oil) affecting the cleanability of different surfaces is discussed in detail.

6.4.1. Factors related to the frying surface in contact

Surface material

The frying experiments with different foods can be categorized as follows:

(i) frying without oil at 200^{o}C

(ii) frying with oil at 200^{o}C

(iii) frying without oil at 240^{o}C

(iv) frying with oil at 240^{o}C

In all the above mentioned categories, there are three common subcategories: (a) frying meat (b) frying carrot (c) frying potato. The results from all the different categories were analyzed in such a way that the performance of different surface materials was evaluated in comparison to stainless steel (reference). A pair-wise student's t-test was employed for this purpose where the cleaning ratings of each surface material were compared with the ratings of stainless steel; the results are shown in Table 6.4 and 6.5. The mean standard deviation derived from the whole set of experiments was used as the standard deviation, commonly for all the following t-test's.

Table 6.4. Cleanability of different surfaces compared with stainless steel after frying at 200^{o}C

Coating Material	Without oil			With oil		
	Meat	Carrot	Potato	Meat	Carrot	Potato
TiAlN (UP 316 SS)	ns	ns	ns	ns	ns	ns
ZrN (UP 316 SS)	ns	ns	ns	↑*	ns	ns
ZrO_2 (UP 316 SS)	ns	ns	ns	ns	↑*	ns
TiAlN (EP 316 SS)	ns	↑*	ns	↑**	↑**	ns
ZrN (EP 316 SS)	ns	ns	ns	↑*	↑**	ns
ZrO_2 (EP 316 SS)	ns	ns	ns	↑*	↑**	ns
QC A5 PM	↑*	↑*	ns	↑**	↑**	↑*
Silicone	↑*	ns	ns	↑**	↑**	↑*
PTFE	↑**	↑**	ns	↑**	↑**	↑*

Average standard deviation on ratings - 0.61

Pairwise t-test 2 x 4 d. f. = 8

ns - not significant

↑ - significantly better cleanability than stainless steel

*p<0.05

**p<0.01

Table 6.5. Cleanability of different surfaces compared with stainless steel after frying at 240^{o}C

Coating Material	Without oil			With oil		
	Meat	Carrot	Potato	Meat	Carrot	Potato
TiAlN (UP 316 SS)	ns	↑**	ns	ns	ns	↑**
ZrN (UP 316 SS)	ns	ns	ns	↑**	ns	ns
ZrO_2 (UP 316 SS)	ns	ns	ns	↑**	ns	ns
TiAlN (EP 316 SS)	↑*	↑**	ns	↑**	↑*	↑**
ZrN (EP 316 SS)	ns	↑**	ns	↑**	↑**	↑**
ZrO_2 (EP 316 SS)	↑*	↑**	↑*	↑**	↑**	↑**
QC A5 PM	↑**	↑**	ns	↑**	↑*	↑**
Silicone	↑**	↑*	↑*	↑**	↑**	↑**
PTFE	↑**	↑**	↑*	↑**	↑**	↑**

Average standard deviation on ratings - 0.61

Pair-wise t-test 2 x 4 d. f. = 8

ns - not significant

↑ - significantly better cleanability than stainless steel

*$p<0.05$

**$p<0.01$

Surface treatment

In order to study the effect of surface treatment on the cleanability, the cleaning ratings of the three different ceramics (TiAlN, ZrN and ZrO_2) coated on unpolished steel were compared with the ratings of ceramics coated on polished steel by means of a pair-wise student's t-test and the results are shown in Table 6.6.

Table 6.6. Effect of surface treatment on cleanability of different surfaces

Surface Material	Temperature (^{o}C)	Without oil			With oil		
		Meat	Carrot	Potato	Meat	Carrot	Potato
TiAlN	200	ns	ns	ns	↑*	↑*	ns
	240	ns	ns	ns	ns	↑*	↑*
ZrN	200	ns	ns	ns	ns	ns	ns
	240	ns	↑*	ns	ns	↑*	↑*
ZrO_2	200	ns	ns	ns	ns	ns	ns
	240	ns	↑*	ns	ns	ns	ns

Average standard deviaition on ratings - 0.61

Pair-wise t-test 2 x 4 d. f. = 8

ns - not significant

↑ - surface material coated on polished steel showed better cleanability

*$p<0.05$

Surface roughness

In addition to the chemistry and nature of the surface material, roughness of a surface is an important factor in determining the cleanability of a surface (Boulange-Petermann, 1996; Wirtanen, 1995). In many studies concerning fouling in the food industry, roughness has always been considered as a major factor affecting the cleanability of different surfaces in the removal of bacteria (Hilbert et al. 2003; Flint et al. 2000; Ortega et al. 2010; Whitehead and Verran, 2006) and biofilms (Wirtanen, 1995). In all these studies, the roughness of a surface is usually characterized by the roughness parameter (R_a). In order to analyze the influence of measured roughness parameter (R_a) (Table 3.1) on the cleanability of different surfaces, a correlation analysis was carried out by plotting the cleaning ratings obtained for different surfaces in each category versus their respective R_a values. For example, the cleaning ratings for different surfaces, following the frying experiments with turkey meat at 200°C, were plotted against their respective roughness parameter (R_a) as shown in Figure 6.1.

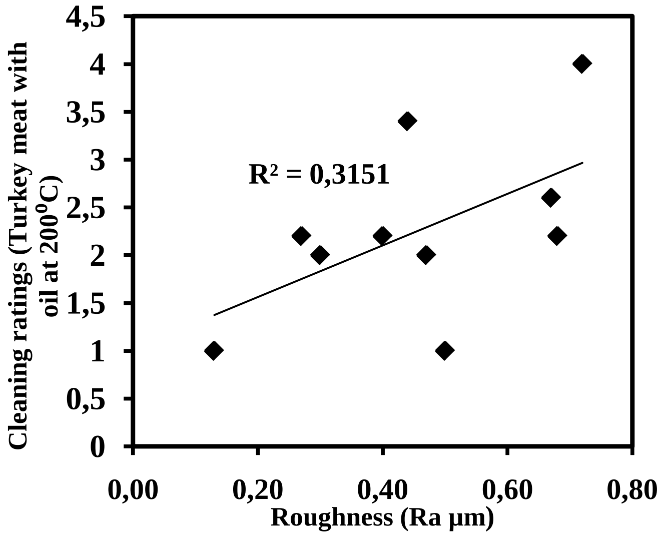


Figure 6.1. Plot of roughness parameter (R_a) versus the cleaning ratings (turkey meat with oil at 200°C) for different surfaces

6.4.2. Factors related to the frying process

Food type

The influence of food type on the cleanability was tested by frying three different kinds of foods: turkey meat, carrot, sweet potato which is varying in composition. In this case, frying a food with and without oil can be considered as two different kinds; according to this, there are six different food types as can be seen from Table 6.7. To analyze the effect of food type, the cleaning ratings obtained for all the surfaces after frying a particular food at a particular temperature were summed up and the mean cleaning rating was calculated. The food types were ranked according to the mean cleaning rating obtained and the results are shown in Table 6.7; the higher the cleaning rating the higher the ranking and vice-versa.

Table 6.7. Influence of left over deposits from frying different foods on the cleanability of different surfaces

Ranking	Frying temperature	
	200°C	240°C
1	Meat (+)	Carrot (+)
2	Carrot (+)	Meat (+)
3	Carrot (-)	Carrot (-)
4	Meat (-)	Potato (+)
5	Potato (+)	Meat (-)
6	Potato (-)	Potato (-)

(+) - Frying with oil

(-) - Frying without oil

1 - better influence on cleanability

6 - poorer influence on cleanability

Temperature

The frying experiments were carried out at two different temperatures in order to test the influence of temperature on the cleanability of different surfaces. In this case, there are two different categories: (i) frying with oil and (ii) frying without oil. The effect of temperature was tested for both these categories by comparing the cleaning ratings obtained at 200°C and 240°C for different surfaces by a pair-wise student's t-test and the results are shown in Table 6.8.

Oil

To test the effect of frying oil on the cleanability of different surfaces, the frying experiments were carried out with and without the use of oil; the influence of oil on the cleanability was tested for the two different categories: (i) frying at 200°C (ii) frying at 240°C by comparing the cleaning ratings obtained with and without the use of oil for different surfaces by a pairwise student's t-test and the results are shown in Table 6.9.

Table 6.8. Influence of temperature on the cleanability of different surfaces after frying with and without the use of oil

Coating Material	Without oil			With oil		
	Meat	Carrot	Potato	Meat	Carrot	Potato
UP 316 SS	ns	**↓	ns	**↓	*↓	**↓
TiAlN (UP 316 SS)	ns	ns	ns	ns	**↓	ns
ZrN (UP 316 SS)	ns	*↓	ns	*↓	**↓	**↓
ZrO_2 (UP 316 SS)	ns	**↓	ns	ns	**↓	**↓
TiAlN (EP 316 SS)	ns	ns	ns	**↓	**↓	ns
ZrN (EP 316 SS)	ns	ns	ns	*↓	ns	*↓
ZrO_2 (EP 316 SS)	ns	ns	ns	*↓	**↓	*↓
QC A5 PM	ns	ns	ns	*↓	**↓	ns
Silicone	ns	*↓	ns	ns	ns	ns
PTFE	ns	ns	ns	ns	ns	ns

Average standard deviaiton on ratings - 0.61

Pair-wise t-test 2 x 4 d. f. = 8

ns - Not significant

↑ - Better cleanability

↓ - Poorer cleanability

*$p<0.05$

**$p<0.01$

Table 6.9. Influence of oil on the cleanability of different surfaces after frying at different temperatures

Coating Material	200°C			240°C		
	Meat	Carrot	Potato	Meat	Carrot	Potato
UP 316 SS	*↓	ns	ns	**↓	ns	**↓
TiAlN (UP 316 SS)	**↓	*↓	*↓	**↓	**↓	ns
ZrN (UP 316 SS)	ns	ns	ns	ns	*↓	**↓
ZrO_2 (UP 316 SS)	ns	ns	ns	ns	ns	**↓
TiAlN (EP 316 SS)	ns	ns	ns	**↓	*↓	ns
ZrN (EP 316 SS)	ns	ns	ns	*↓	ns	*↓
ZrO_2 (EP 316 SS)	ns	ns	ns	**↓	ns	**↓
QC A5 PM	ns	ns	ns	**↓	**↓	ns
Silicone	ns	ns	ns	ns	**↑	ns
PTFE	ns	ns	ns	ns	ns	ns

Average standard deviation on ratings - 0.61

Pair-wise t-test 2 x 4 d. f. = 8

ns - Not significant

↑ - Better cleanability

↓ - Poorer cleanability

*$p<0.05$

**$p<0.01$

Discussion

The cleanability of ceramics (deposited on unpolished steel) in most cases was not better than stainless steel as shown in Table 6.4 and 6.5. A difference in their performances was noticed following the frying experiments with oil at 240^{o}C; however, the difference was significant only for some combinations of food and material (Table 6.5). Some of the ceramics showed a better performance than stainless steel since the oil deposits were easier to clean from them. There is a significant difference in the cleanability of stainless steel and ceramics (deposited on polished steel) in all the experiments except the cleaning ratings obtained, following the frying experiments without oil at 200 ^{o}C; in this case, the difference in their surface topography played a significant role on their varied performances. The performances of quasicrystalline (QC (Al, Fe, Cr)), silicone and PTFE were significantly better than stainless steel in almost all the experiments (Table 6.4 and 6.5).

When analyzing the effect of surface treatment on the cleanability, it was found that TiAlN (EP 316 SS) was easier to clean than TiAlN (UP 316 SS) following the frying experiments with different foods with oil at different temperatures (Table 6.6). The oil deposits remaining on a smooth surface were easier to clean than the deposits adhered to a rough surface. In case of zirconium based ceramics, the surface treatment is effective while cleaning the deposits from frying of carrot (Table 6.6). Numerically, all the cleaning ratings for the ceramics coated on electropolished steel are lower or identical to the ceramics coated on unpolished steel. However, the difference is significant only for some combinations of food and material.

It was found by many authors that there is no direct correlation between the roughness parameter (R_a) and the cleanability; a distinct correlation could not be achieved between the roughness parameter and the cleanability since the exact topographic profile of a material could not be determined by these types of roughness parameters (Hilbert et al., 2003; Holah and Thorpe, 1990; Mettler and Carpentier, 1999; Taylor and Holah, 1996; Yoon and Lund 1994. The correlation analysis, carried out separately for each different category of a frying and cleaning experiment, between the roughness parameter and the cleaning ratings obtained for different surfaces indicates that the roughness parameter (R_a) measured for a surface cannot directly indicate its cleanability.

The results from Table 6.7 indicates that a grouping of different foods is possible based on their influence on the cleanability of different surfaces: food types from ranking 1 - 3 with a stronger influence on the cleanability can be placed in one group (first) and foods from ranking 4 - 6 with a weaker influence on the cleanability can be placed in another group (second). The deposits from frying carrot and turkey meat produced a stronger influence on the cleanability and hence, occupied the first group. The frying deposits of sweet potato produced a weaker influence on the cleanability and hence, occupied the second group. The stronger influence of the frying deposits of carrot on the cleanability could be due to the high content of reducing sugar in carrot (Table 6.1); at high frying temperatures, reactions such as caramelization and decomposition of sugar will take place in carrot resulting in typical brown and black coloured deposits adhering to the frying surfaces thereafter hindering the surface cleanability. The results also indicate that the deposits resulting from frying meat with oil produced a stronger effect on the cleanability; but, the deposits left after frying meat without oil showed a weaker effect on the cleanability. Due to the high reactivity of proteins at temperatures above 80^{o}C, they react among themselves to form networks; in addition, they react with the metal ions present in the frying surface (Barham, 2001). The initial protein fouling starts with adhesion to the surface at room temperature; when they are heated, the resulting fouling layers can form bonding with the initially formed protein layer hindering the cleanability of the surfaces (Rosmaninho, et al., 2007).

It can be seen from Table 6.8 that the temperature does not significantly influence the cleanability of different surfaces if the frying experiments were performed without the use of oil; however, the temperature produced a stronger influence on the cleanability of different surfaces following the frying experiments with oil. These results lay strong emphasis on the reactions of oil taking place at high frying temperatures, which will be described in the following section.

Contact frying process is normally accompanied by the use of oil as a frying medium (Soupas et al. 2007); however, the frying oil has significantly decreased the cleanability of different surfaces when frying was carried out at high temperature (240^{o}C) (Table 6.9). The oil used in the frying process undergoes a series of physical and chemical reactions such as hydrolysis, oxidation and thermal decomposition (Santos et al. 2004; Soupas et al. 2007; Orthoefer and Cooper, 1996). The mechanism for the thermally induced reactions in methyl oleate (an ester of oleic acid; oleic acid is the main constituent of olive oil) during heating was proposed by Sen Gupta (1967). The frying experiments, in this case, were carried out using rapeseed oil which is rich in monounsaturated fatty acids (Santos et al. 2004. Since oil decomposition generally proceeds through a free radical mechanism (Santos et al.2004), the proposed thermal reactions in rapeseed oil (Figure 6.2 and 6.3) follows the free radical mechanism proposed by Sen Gupta (1967). The thermal reactions in rapeseed oil occurs in two steps: (i) The homolytic splitting at positions alpha to the double bond (exemplified here with erucic acid) can result in the formation of free radicals (Figure 61) (ii) The free radicals formed in the first step can abstract hydrogen atom from a new molecule of erucic acid resulting in the formation of an unsaturated radical and myristic acid; the unsaturated radical reacts with the radicals (I and III) to give the final compounds (Figure 6.2). These products resulted during the frying process with oil could directly deposit on the frying surface where it is likely to react with the metal ions present in the frying surface causing covalent bonds with the surface. Likewise, free fatty acids are formed from both hydrolysis and oxidation reactions in the oil during heating (Nawar, 1969; Orthoefer and Cooper, 1996); the formed acid could also directly react with the active metal surface resulting in covalent bonds to the surface. Furthermore, the products formed by the acid attack on the surface can act as a catalyst for the polymerization of the unsaturated fatty acids; principally, the fat could polymerize on the frying surface hindering the cleaning properties of the surface.

Figure 6.2. Formation of free radicals from erucic acid by heating

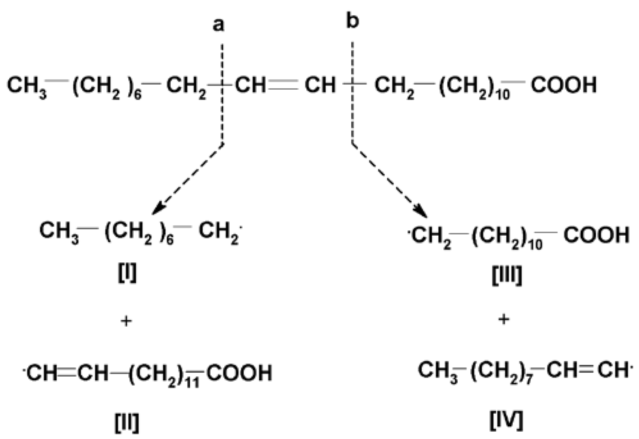
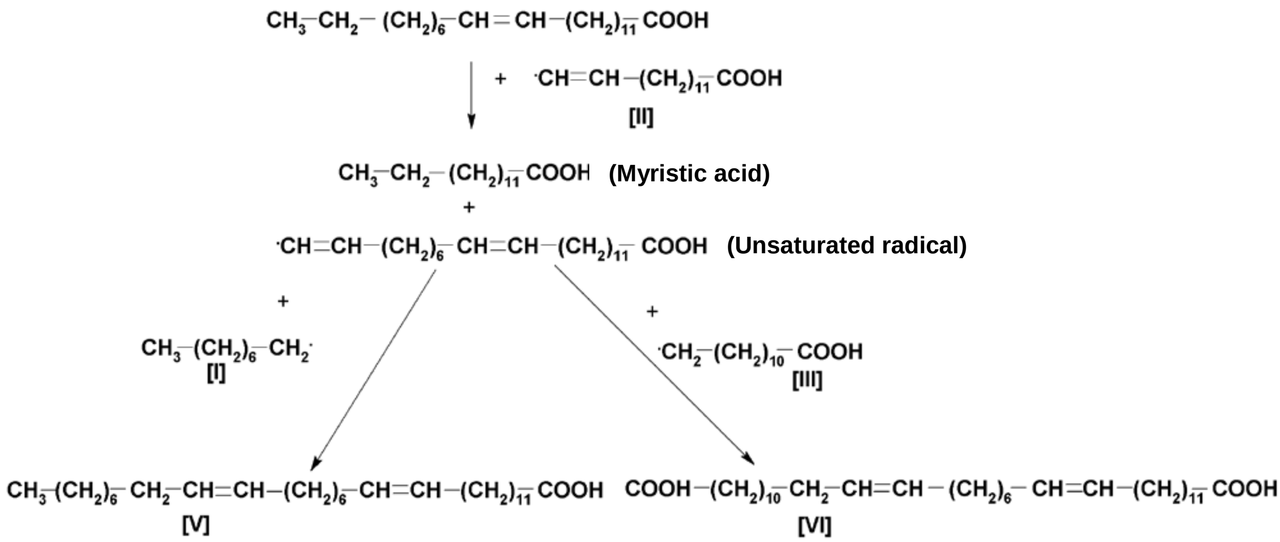


Figure 6.3. Abstraction of hydrogen from erucic acid and formation of high-molecular weight products



The outcome of these frying and cleaning experiments has many interesting indications for testing the cleanability of contact frying surfaces. The property of a good frying surface is exemplified by its wetting properties with oil; the surface which possesses good wettability with oil is recommended for the frying process. It is, however, demonstrated in our studies that the use of oil for the frying process has produced a significant effect on the cleanability of the frying surfaces; the significant influence of oil on the cleanability was reflected in all our results. It is therefore whenever new materials are selected for frying equipments, one should be aware of the fact that the material which is good for frying purposes may not necessarily be good for easy clean purposes too.

The results also exemplify the complexity of the fouling mechanism in contact frying. It is clearly demonstrated from our results that in case of frying where the frying surface is in direct contact with the food, the level of cleanability is affected not only by the surface chemistry and topography of the frying surface in contact but also by the type and the chemical composition of food and the nature of the thermally induced reactions. The occurrence of the thermally induced reactions such as caramelization, maillard browning and protein denaturation cannot be avoided; these reactions are, however, desirable to achieve the right sensory quality of the food.

6.5. Cleaning treatment after contact baking of pancake

The different surfaces following the frying experiments with pancake (section 5.3.4) were cleaned using a commercial alkaline detergent (Sunlight Citrus, Unilever Denmark, Copenhagen, Denmark). The frying experiments with pancake on different surfaces left with residues which were not as intense as in contact frying experiments with the foods; therefore, a chemical soaking procedure was not included in these cleaning tests where a simple mechanical cleaning will be sufficient to remove the stains. A numerical rating procedure similar to Groll (2006) was used to describe the cleanability of different surfaces:

1 - The stains are removed by rinsing with running water for one minute

2 - The stains are removed with detergent using a household cleaning sponge by moving firmly on the surface

3 - The stains are removed with detergent using a household cleaning sponge with slight force

4 - The stains are removed with detergent using a household cleaning sponge with intense force

5 -The stains are difficult to remove with detergent using a household cleaning sponge so a scotch-brite® must be used to remove the stains

Table 6.10. Cleaning ratings for different surfaces after pancake frying at different temperatures

Surface	Set temperature (^oC)	Cleaning ratings (five repetitions)		
		Frying rig		
		Mean	Minimum	Maximum
Teflon (Al Mg 5754)	160	1.0	1	1
	200	1.0	1	1
	240	1.0	1	1
Aluminium Al Mg 5754	160	2.2	2	3
	200	3.0	3	3
	240	3.6	3	4
316 Stainless Steel	160	2.0	2	2
	200	2.8	2	3
	240	4.0	4	4
TiAlN (UP 316 SS)	160	2.0	2	2
	200	3.0	3	3
	240	2.0	2	2
ZrN (UP 316 SS)	160	2.0	2	2
	200	3.0	3	3
	240	3.0	3	3
ZrO_2 (UP 316 SS)	160	2.0	2	2
	200	3.0	3	3
	240	3.6	3	4
TiAlN (EP 316 SS)	160	3.6	2	4
	200	3.0	3	3
	240	2.8	2	3
ZrN (EP 316 SS)	160	4.0	4	4
	200	3.0	3	3
	240	4.0	4	4
ZrO_2 (EP 316 SS)	160	4.0	4	4
	200	3.0	3	3
	240	4.0	4	4

Standard deviaition on the means of ratings (five repetitions) - 0.13

6.5.1. Factors affecting the cleanability of different surfaces

Temperature ($F = 50$; d.f. = 2, 92; $P < 0.001$) and surface material ($F = 37$; d.f. = 7, 92; $P < 0.001$) produced a significant effect on the cleaning ratings of different surfaces as can be seen from Table 6.10. When the cleaning ratings of stainless steel and aluminium were compared with each other, there is no difference in their cleanability as can be seen from Table 6.10. It is clear from Table 6.10

that the difference in ceramic material composition i.e., TiAlN, ZrN or ZrO_2 does not produce any significant difference on the cleaning ratings at 160 and 200°C. However, the cleanability of TiAlN ceramic material seems to be different from ZrN or ZrO_2 at 240°C. When the cleaning ratings of ceramics coated on unpolished steel were compared with the ratings of stainless steel, yet again no difference can be seen between them at 160 and 200°C. Yet, it is interesting to note that TiAlN (UP 316 SS) shows better cleanability than stainless steel at 240°C and ZrN (UP 316 SS) seems to be different from stainless steel at 240°C.

It is clear from Table 6.10 that the cleaning ratings of stainless steel and aluminium increases with increase in temperature; this trend cannot be observed with ceramics because their ratings vary with rise in temperature. The effect of topography was reflected in the cleaning tests where ceramics deposited on unpolished steel obtained lower cleaning ratings than the ceramics deposited on polished steel, as shown in Table 6.10. As shown in Table 6.11, surface topography produced significant effect on the cleaning ratings at 160 and 240°C; there is no such effect at 200°C since the cleaning ratings obtained for ceramics deposited on unpolished and polished steel were similar at 200°C.

Table 6.11. Calculated F-values from ANOVAs to analyze the effect of roughness on data from Table 6.10

Method	Set temperature (° C)	Factor	F	Degrees of freedom	Significance
Cleaning rating	160	Ceramic Surfaces	1.00	4, 20	$P > 0.05$
		Roughness	196	1, 20	$P < 0.001$
		Interaction	1.00	2, 20	$P > 0.05$
		Reproducibility	1.00	4, 20	$P > 0.05$
	240	Ceramic Surfaces	74	4, 20	$P < 0.001$
		Roughness	55	1, 20	$P < 0.001$
		Interaction	3.18	2, 20	$P > 0.05$
		Reproducibility	1.82	4, 20	$P > 0.05$

6.5.2. Cleaning ratings for different surfaces on the frying rig and in the oven

Table 6.10 shows the cleaning ratings of different surfaces following the pancake frying experiments with different surfaces tested on the frying rig (section 2.3 in paper I) as well as in a household convection-oven (section 2.6 in paper I). PTFE obtained a rating of one in all cases, both on the frying rig and in the oven. The cleaning rating is five for all surfaces (except PTFE) at all temperatures when tested in the oven; however, the cleanability of the same surfaces varied to a great extent when testing on the frying rig (Table 6.10). This again emphasizes the advantages of using frying rig for analyzing different surfaces for contact frying processes.

6.5.3. The release rating and the cleaning rating

The release ratings for different surfaces are shown in Table 5.5 and the cleaning ratings for different surfaces are shown in Table 6.10. The data are plotted against each other in figure 6.4. The figure shows that there is a good linear correlation between release rating and cleaning rating (R^2=0.78). It is apparent from our results that the surfaces which showed good non-stick properties with pancake also demonstrated good easy-to-clean properties. In case where the pancake sticks firmly to the frying surface, the residuals left on the surface are also difficult to clean subsequently. Whenever the food adheres to a surface, there arises a need to clean the surface; if the strength of adhesion between the food and the surface is poor it results in easy cleaning and vice-versa.

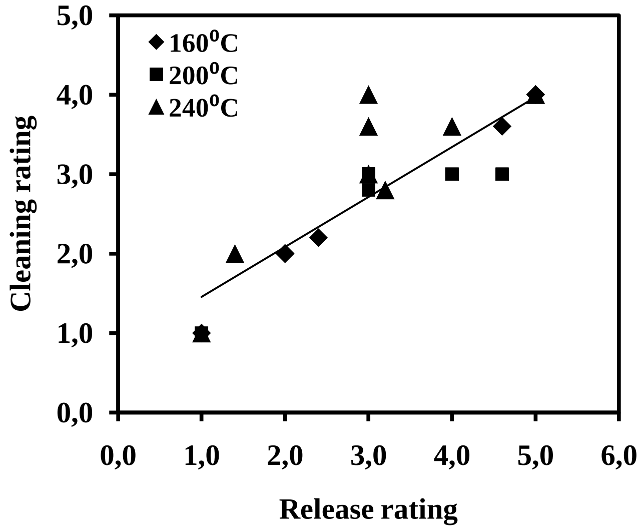


Figure 6.4. Plot of release rating versus cleaning rating

6.6. Conclusion

The cleaning experiments performed with different food models yielded distinct results. When the cleaning experiments were performed with pancake as the food model, the ceramics deposited on electro-polished stainless steel showed poorer performance than the ceramics deposited on unpolished stainless steel. In contrast to the above results, the ceramics deposited on polished steel showed better cleaning properties than ceramics deposited on unpolished steel when they were tested for frying turkey meat, carrots and sweet potatoes. The complexity of the fouling mechanism in contact frying is apparently demonstrated by the varied results achieved from these frying and cleaning experiments; however in both cases, surface topography played a significant role on the cleaning properties of different surfaces.

CHAPTER 7

CLEANABILITY EXAMINATION OF DIFFERENT SURFACES USING SEM AND CONTACT ANGLE MEASUREMENTS

7.1. Scanning Electron Microscopy (SEM)

The cleanability of a surface is affected by the size and type of surface irregularity (Hilbert et al. 2003). The roughness parameter of a surface (R_a) measured using the surface profilometer will, however, only give very little information about the true topography of a surface and the presence of porosities or scratches (Hilbert et al. 2003). Thus, it is always not easy to correlate the cleaning efficiency only with the roughness measurements – unlike what was the case with the sticking properties as shown in Chapter 5. Techniques like scanning electron microscopy (SEM) are therefore needed to characterize in more detail the topographic profile and defects of the surface in order to provide any useful information regarding the surface cleanability.

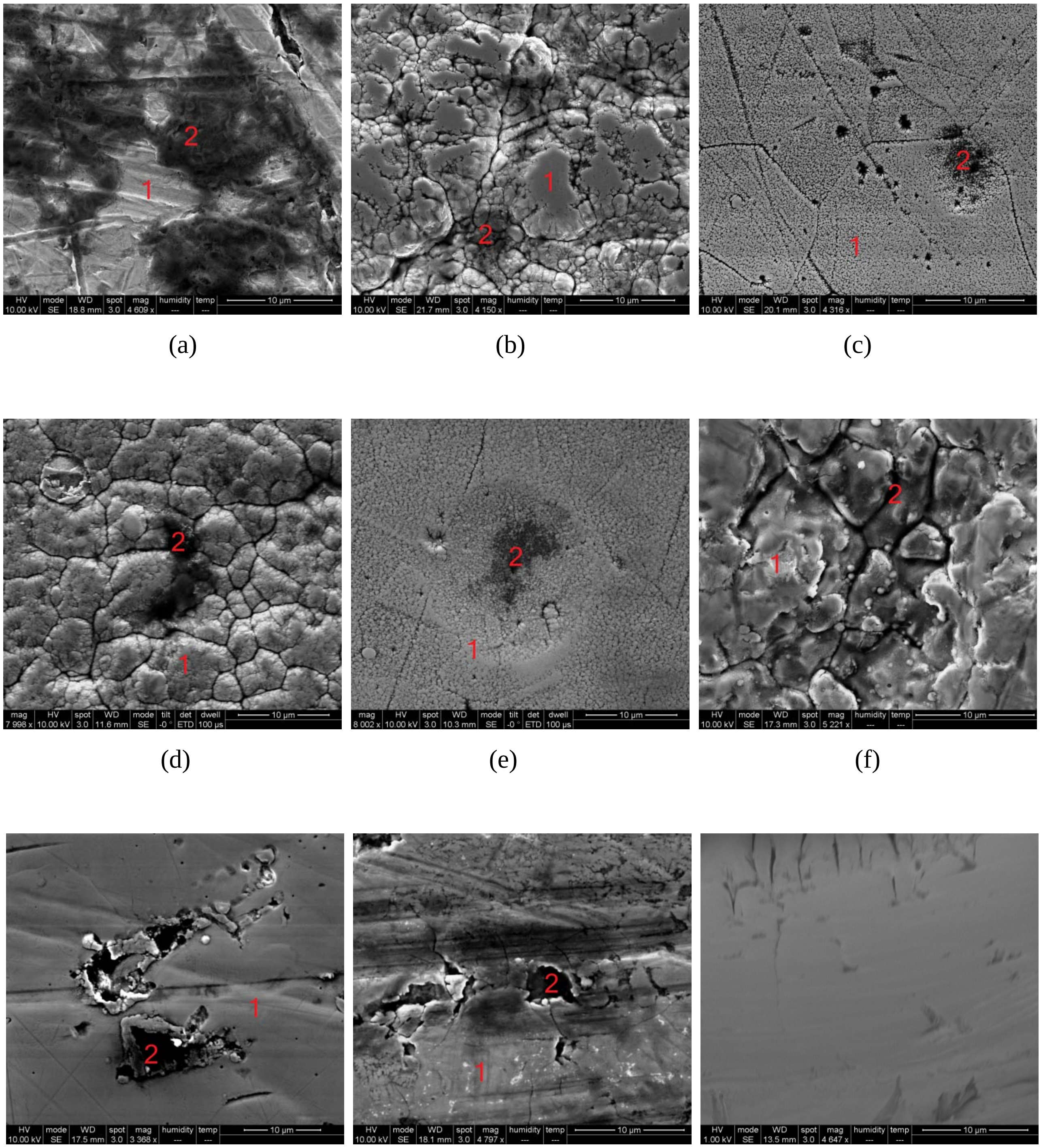
In cleanability investigation of food contact surfaces, it is normally required to characterize the surfaces as well as the deposits adhering to them. A direct observation of the surfaces is needed in order to assure that the surfaces are really clean without any deposits adsorbed on them (Leclercq-Perlat and Lalande, 1994). The adhesion of food products is also commonly evaluated by direct observations (Michalski et al. 1997), however more information can be gained from a knowledge of the composition of the residuals remaining on a surface after the cleaning process (Verran et al., 2008). Moreover, by identifying the nature and amount of residuals present on the surface, the efficiency of the cleaning procedure can be understood (Almäs and Lund, 1984).

SEM is a useful technique to visually inspect the residuals left on a surface and can be used as a (semi) quantitative technique for elemental composition (Hilbert et al., 2003) of the surfaces or the deposits attached to them. SEM has been used to visualize and analyze cleaned stainless steel and heat exchanger surfaces and the milk deposits attached to them (Almäs and Lund, 1984; Narataruksa et al. 2010; Tissier and Lalande, 1986); SEM (environmental scanning electron microscope) together with XPS was used to analyze the cleaned stainless steel and ceramic surfaces fouled using a milk powder soil (Verran et al. 2001).

The evaluation methods or testing procedures can be made more realistic by including continuous cleaning and soiling procedures similar to food factory situations where build up of deposits or microorganisms will occur only after several times of usage of any food process equipment (Verran et al., 2001). In the present work, the different surfaces were therefore re-used after each frying experiment, and after completion of the whole set of experiments (see Chapter 6) they were cleaned and analyzed by SEM.

In the present work, the photomicrographs were taken with a field emission gun scanning electron microscope (FEGSEM 200F) using an accelerating voltage of 10 kV for all the examinations. The micrographs allowing a visual observation of the cleaned surfaces using SEM are shown in Figure 7.1. The cleaned surfaces when analyzing using SEM showed some areas which were dark and stained (indicated as no. 2 in Figure 7.1) while other areas were normal and unstained (indicated as no. 1 in Figure 7.1). Since it is of interest and informative to know the compositional difference between the stained and unstained areas, an elemental analysis was performed at these two areas using energy dispersive spectroscopy (EDS). Three such spots were identified in each frying surface and the average composition of the three spots is shown in Table 7.1. The elemental analysis and the data interpretation are in a similar way to the methods followed in the literature (Almäs and Lund, 1984; Verran et al. 2001). During the elemental analysis of the stained and unstained areas, if elements characteristic of foods but not present in the original composition of the surface material were detected these would probably have originated from the food constituents during frying or cleaning chemicals used in the cleaning process.

The silicone coated on anodized aluminium surface was cleaned using the normal cleaning procedure, as described in section 6.4.3, expecting that the anodized aluminium substrate could resist the mild alkali conditions prevailed during the cleaning procedure. However in due course, dark black colour stains emerged out on the silicone coated surface suggesting that the underlying anodized aluminium substrate could have been attacked by the alkali. It is therefore the silicone coated surface was not analyzed in SEM. In the following section, the results from the compositional analysis of different cleaned frying surfaces are discussed in detail.



(a) (b) (c)

(d) (e) (f)

(g) (h) (i)

Fig 7.1 Morphology of different cleaned surfaces illustrating the unstained (1) and stained (2) areas (a) stainless steel (b) TiAlN (UP 316 SS) (c) TiAlN (EP 316 SS) (d) ZrN (UP 316 SS) (e) ZrN (EP 316 SS) (f) ZrO_2 (UP 316 SS) (g) ZrO_2 (EP 316 SS) (h) QC (Al, Fe, Cr) (i) PTFE. All pictures are taken with the same magnification (note the 10µ bar in the bottom of each picture).

Table 7.1. Chemical composition of the unstained (1) and stained areas (2), as determined by energy dispersive spectroscopy

Elements (at. %)	Surface Material							
	UP 316 SS	TiAlN (UP 316 SS)	TiAlN (EP 316 SS)	ZrN (UP 316 SS)	ZrN (EP 316 SS)	ZrO_2 (UP 316 SS)	ZrO_2 (EP 316 SS)	QC (Al, Fe, Cr)
Unstained areas (1)								
Fe	58.6 ± 2.7	0	0	0	0	0	0	10.4 ± 3.7
Cr	18.2 ± 2.6	0	0	0	0	0	0	11.4 ± 2.7
Ni	15.0 ± 1.8	0	0	0	0	0	0	0
O*	8.1 ± 1.7	0	0	0	0	68.5 ± 2.5	69.3 ± 1.2	54.7 ± 3.4
Ti	0	24.6 ± 1.2	25.3 ± 2.1	0	0	0	0	0
Zr	0	0	0	44.4 ± 3.0	41.5 ± 2.1	31.5 ± 2.5	30.6 ± 1.2	0
Al	0	22.9 ± 1.9	26.3 ± 1.2	0	0	0	0	23.5 ± 3.5
N*	0	52.4 ± 3.0	48.4 ± 3.3	55.6 ± 3.0	58.5 ± 2.1	0	0	0
Stained areas (2)								
Fe	17.3 ± 2.2	0	0	0	0	0	0	0
Cr	6.7 ± 1.6	0	0	0	0	0	0	11.0 ± 1.4
Ni	0	0	0	0	0	0	0	0
O*	45.2 ± 3.5	0	0	19.2 ± 3.1	12.0 ± 3.5	29 ± 3.3	36.0 ± 3.4	18.8 ± 4.0
P	9.1 ± 1.1	0	0	0	0	0	0	5.8 ± 1.1
K	4.8 ± 1.0	0	0	0	0	0	0	3.0 ± 1.0
Na	3.5 ± 1.0	0	0	0	0	0	0	-
Mg	3.6 ± 1.1	0	0	0	0	0	0	2.1 ± 0.7
C*	9.8 ± 1.9	33.8 ± 3.7	28.00 ± 3.74	51.7 ± 4.0	39.1 ± 4.4	56.4 ± 4.0	42.7 ± 4.1	37.4 ± 5.3
Ti	0	13.6 ± 1.0	14.62 ± 0.42	0	0	0	0	0
Zr	0	0	0	11.1 ± 1.3	25.4 ± 1.8	14.6 ± 2.3	21.3 ± 2.0	0
Al	0	16.9 ± 1.8	20.00 ± 1.24	0	0	0	0	21.9 ± 3.1
N*	0	35.6 ± 3.0	37.38 ± 2.97	18.0 ± 1.6	23.5 ± 3.8	0	0	0

* measured values may not be accurate since the elements possess low atomic numbers

7.1.1. Composition of the cleaned frying surfaces

Stainless steel

The topography of the cleaned stainless steel surface is shown in Figure 7.1a. Elements such as iron, chromium, nickel and oxygen were detected when the unstained areas on the stainless steel surface were examined. The presence of oxygen confirms the formation of an oxide layer on top of the stainless steel surface exposed to atmosphere. The elements: Fe, Cr and Ni detected at the unstained areas are the main constituents of stainless steel. The figure 7.1a clearly illustrates that a residual film remains attached to the stainless steel surface even after the cleaning process; many non-metallic elements with C and P as the most abundant were detected when the composition of the residual film was analyzed (Table 7.1). The elements C, P, K, Na, and Mg detected at the residual film must have been deposited when the stainless steel surface was exposed to frying with different food types which are rich in these types of involatile elements (Pennington and Youngt, 1990) (Isherwood and King 1976; Sherman and Mehta, 2009).The residual film adhered to the stainless steel surface may largely stem from meat deposits since the protein molecules have a general affinity to adsorb onto stainless steel surfaces, even at room temperature (Rosmaninho et al. 2007). Electrostatic adhesion is proposed to be responsible for the adhesion of proteins to surfaces, especially stainless steel (Nassauer and Kessler, 1987; Michalski et al. 1997).

Ceramics

The topography of the cleaned TiAlN (UP 316 SS) and TiAlN (EP 316 SS) ceramics are shown in Figure 7.1b and 7.1c. The analysis of the unstained areas showed the presence of elements such as titanium, aluminium and nitrogen (Table 7.1); these elements represent the elemental composition of TiAlN coating. Carbon was the only contaminant present at the stained areas.

The topography of the cleaned ZrN (UP 316 SS) and ZrN (EP 316 SS) ceramics are shown in Figure 7.1d and 7.1e. The analysis of the unstained areas revealed the elemental composition of ZrN coating (zirconium and nitride). When the composition of stained areas was analyzed, it was found that carbon and oxygen were present as main contaminants at the stained areas.

The topography of the cleaned ZrO_2 (UP 316 SS) and ZrO_2 (EP 316 SS) ceramics are shown in Figure 7.1f and 7.1g. The elemental composition analysis showed that only zirconium and oxygen were present at the unstained areas. When analyzing the composition of stained areas, it was found that carbon was a main contaminant present at those areas.

Quasicrystalline

The topography of the cleaned QC (Al, Fe, Cr) is shown in Figure 7.1h. The quasicrystalline coating material used in the present study consists of elements such as iron (Fe), chromium (Cr) and aluminium (Al). The detection of these elements Fe, Cr, Al and O at the unstained areas clearly indicates that oxygen was present as a contaminant at those areas. However, the analyses of the stained areas or defects in the surface showed the presence of many elements, with C as the most abundant see Table 7.1. The existence of C and other elements such as P, K and Mg suggests that the deposits resulting from frying different foods, particularly meat remain attached to the surface defects and serve as a potential contaminant.

PTFE

The morphology of the PTFE surface indicates that no such stained areas can be detected as shown in Figure 7.1i. The elemental composition of different regions on the PTFE surface is C = 17.6 ± 3.8; F = 54.3 ± 5.4; O = 28 ± 3.66. The detection of oxygen indicates that oxygen is present as a contaminant on the PTFE surface. The absence of elements Na, K, and P indicates that there were no detectable food residues remain attached to the PTFE surface.

7.1.2. Chemical composition and topography of the cleaned frying surfaces

The carbon deposits were left over the frying surface as the result of the pyrolysis of the food constituents during the frying process (Chicester, 1981). Since carbon is insoluble in water, these types of deposits could not be easily removed from the frying surfaces by cleaning with water or detergents. Generally, the salts such as potassium and sodium are readily soluble in water. If these types of salts were remaining on the frying surface as a consequence of the thermally induced reactions in food, they could be readily removed from the frying surface by simple rinsing with water. However, these types of non-metallic elements such as potassium, sodium, phosphorus were detected on the stainless steel as well as on quasicrystalline material, even after the surfaces were cleaned. This shows that the elements were bound to such surfaces and hence, could not be washed away from the surfaces during the cleaning process.

The findings demonstrate that whilst stainless steel and quasicrystalline surfaces show several impurities in addition to the carbon contamination, this was not the case for ceramics since carbon was the only main contaminant present on ceramics. Since all the different surfaces were subjected to the same type of frying experiments, differences in the composition of impurities adhered to these surfaces could depend on the extent of interaction between the surface material and the contaminant. These results suggest that the interactions occurring between protein molecules (present in meat) and metal ions (present in the frying surface) during the heating process (Barham, 2001) could be responsible for the strong adherence of the deposits to the stainless steel or quasicrystalline surface even after cleaning. The resistance of the ceramics to interact with food components during frying could perhaps result in carbon being the only main impurity present on their surfaces.

Due to increased attachment sites, food residues or impurities gets interlocked within the defects or grooves as a result of the mechanical interlocking phenomenon. It is clear from the SEM micrographs shown in Figure 7.1 that in most of the surfaces, surface defects, grooves and scratches retained more residues and hence were more contaminated than the flat regions. The residues trapped within the surface defects cannot be eliminated by rinsing fluids since they receive less force during cleaning or are less accessible to cleaning resulting in their decreased removal (Boulange-Petermann, 1996; Holah and Thorpe, 1990; Verran et al., 2001); subsequently, ending up in issues related to hygiene and cleanability. Ceramics were found to be easy-clean, inert and abrasion resistance than stainless steel; yet, they were not easy to clean like a PTFE material. Ceramics, although proves to be more inert than stainless steel and quasicrystalline materials, suffered from interlocking phenomenon since carbon deposits were found to be adhered to their grain boundaries or grooves. These results suggest that in addition to surface chemistry, surface topography of the frying surface also play a significant role in deciding the cleanability. The material selected for the frying process should be chemically inert as well as mechanically free of defects in order to reduce the cleaning efforts or to make cleaning easier.

7. 2. Contact angle measurements

It is a standard procedure to evaluate the easy-to-clean properties of different surfaces by measuring their contact angle values with water (Kuisma et al. 2007; Maatta et al. 2007; Handojo et al. 2008; Yoon and Lund, 1994; Yang et al. 1991). In the search for new surface materials for industrial food frying equipments, it is mandatory that the material selected should have easy-release and easy-clean properties, yet also have good surface characteristics for frying. Faulkner (2001) states that "In terms of surface chemistry, a perfect non-stick cookware is one which would be wetted very well by olive oil but it should behave as hydrophobic as possible towards water-based dispersions". On surfaces like PTFE however, the oil form discrete droplets at the interface between food and surface which is not desirable for a good frying process (Faulkner, 2001). In order to select a suitable surface for the frying process, it is essential that the selected surface could wet very well with olive oil. Moreover in chapter 6, where we discussed the cleaning properties of different surfaces following the fouling from contact frying of different foods (carrot, sweet potato, turkey meat) with and without the use of oil, it was revealed that the use of oil for the frying process produced a significant effect on the cleanability of different surfaces. These results also imply that studying the interfacial properties of different surfaces with oil could aid in the process of choosing an appropriate easy-to-clean surface. However, it is not sufficient to measure the contact angle values only at room temperature since the spreading behaviour of a liquid on a solid during high-temperature applications will be different from the same at room temperature; especially for high temperature processes like frying, it is important to study the interfacial properties at the frying temperature. Hence, experiments were carried out to measure the contact angle values of different surfaces with olive oil at different temperatures: 25, 50, 100, 150 and 200^{o}C and the results are shown in Table 7.2. The results shown in Table 7.2 and the following discussion section were extracted from paper II. The results in the form of graphs are shown in paper II; the results are presented here in a tabular form to clearly recognize the contact angle and cos θ values.

Table 7.2. Contact angle of olive oil on different surfaces at different temperatures

Surface Material	Temperature (^{0}C)	Contact Angle (^{0})	cos θ	d(cos θ)/dT * 10^4
UP 316 SS	25	17.4 ± 0.3	0.954	3
	50	16.2 ± 0.4	0.960	
	100	13.2 ± 0.6	0.973	
	150	4.8 ± 0.8	0.996	
	200	0.0 ± 0.0	1.000	
TiAlN (UP 316 SS)	25	14.0 ± 0.9	0.970	2
	50	12.2 ± 0.7	0.977	
	100	5.8 ± 0.4	0.995	
	150	5.0 ± 0.3	0.996	
	200	0.0 ± 0.0	1.000	
TiAlN (EP 316 SS)	25	16.0 ± 0.5	0.961	2
	50	10.4 ± 0.4	0.984	
	100	6.3 ± 0.3	0.994	
	150	4.3 ± 0.5	0.997	
	200	0.0 ± 0.0	1.000	
ZrN (UP 316 SS)	25	9.6 ± 0.4	0.986	0.7
	50	8.6 ± 0.3	0.989	
	100	7.8 ± 0.4	0.991	
	150	5.9 ± 0.5	0.995	
	200	0.0 ± 0.0	1.000	
ZrN (EP 316 SS)	25	15.5 ± 0.3	0.964	2
	50	14.2 ± 0.3	0.969	
	100	11.4 ± 1.0	0.980	
	150	5.3 ± 0.2	0.996	
	200	0.0 ± 0.0	1.000	
ZrO_2 (UP 316 SS)	25	8.5 ± 0.5	0.989	0.6
	50	6.7 ± 0.5	0.993	
	100	5.2 ± 0.1	0.996	
	150	3.9 ± 0.3	0.998	
	200	0.0 ± 0.0	1.000	
ZrO_2 (EP 316 SS)	25	15.8 ± 0.4	0.962	2
	50	13.8 ± 0.9	0.971	
	100	10.3 ± 0.3	0.984	
	150	4.3 ± 0.6	0.997	
	200	0.0 ± 0.0	1.000	

Table 7.2. Contact angle of olive oil on different surfaces at different temperatures (continued from previous page)

Surface Material	Temperature (^{0}C)	Contact Angle (^{0})	cos θ	d(cos θ)/dT * 10^4
QC (Fe, Al, Cr)	25	41.8 ± 0.9	0.746	15
	50	36.4 ± 0.8	0.805	
	100	20.5 ± 1.3	0.937	
	150	9.1 ± 0.6	0.987	
	200	0.0 ± 0.0	1.000	
PTFE	25	67.8 ± 0.8	0.379	9
	50	65.3 ± 0.6	0.418	
	100	62.8 ± 0.4	0.458	
	150	61.2 ± 0.9	0.482	
	200	57.1 ± 0.9	0.543	
Silicone	25	75.3 ± 0.3	0.255	14
	50	66.4 ± 0.6	0.401	
	100	64.3 ± 0.8	0.434	
	150	62.0 ± 0.7	0.470	
	200	56.3 ± 1.0	0.555	

7.2.1. Contact angle and cleanability

Table 7.2 indicates that the difference in the wettability of different surface materials at room temperature is apparent. However, as the temperature rises the difference vanishes between the metals, ceramics and quasicrystalline materials except polymers. The quasicrystalline material has a high contact angle with oil at room temperature and thus one could expect it to be a better easy-to-clean surface than the metal and ceramics. But as the temperature rises, it shows a fast decrease in the contact angle and at 200^{o}C it shows a complete wetting with oil similar to that of the metal and ceramics. As shown in Table 6.3, the cleanability of the quasicrystalline material was similar to the ceramics. The wetting behavior of polymers (PTFE, silicone) was completely different from other materials. While all the other materials show complete wetting with oil at 200^{o}C, the polymers show a high contact angle with oil at 200^{o}C as shown in Table 6.3; this observation is in agreement with Faulkner's statement. In order to achieve a good adhesion between a liquid and a surface, it is necessary that the liquid should completely wet the surface (Allen, 1993). Therefore, it is evident that the poor wetting of polymer surfaces with oil at high temperature generated poor adhesion between the oil and the polymer surfaces at high temperatures, eventually resulting in good easy-to-clean properties (Table 6.3). The good wettability of the surfaces (metal, ceramics and quasicrystalline) with olive oil at high temperatures imply that the adhesion between oil and the surfaces is enhanced at high temperatures. Since these surfaces showed poor cleaning properties with oil (Table 6.3), it could be suggested that if the frying surface has good wetting properties with oil, difficulties may arise in cleaning the surfaces after the frying process. Hence, a correlation analysis was carried out to investigate whether any direct relation exists between the cos θ values and cleaning ratings for the different surfaces at 200^{o}C, as discussed in the following section.In case of frying, the temperature on the frying surface is around 180 - 200 ^{o} C but the temperature on the food surface in contact with the frying surface is lower because the food is cooled by moisture evaporation (Claeys et al. 2005). Therefore, the temperature of the frying oil will be less than the actual frying temperature; the oil temperature in the present work was probably between 100 and 150^{o}C. A correlation analysis was carried out by plotting the cleaning ratings for different surfaces at 200^{o}C (Table 6.3) versus their cos θ values at 100 and 150^{o}C (Table 7.2). A definite correlation could not be obtained between the cleaning ratings and cos θ values at both temperatures. But an association can be seen based on the nature of the material: Polymers possess lower cos θ values at high temperatures and gave lower cleaning ratings (average rating 1.1 - 1.2). Other surfaces (metal, ceramics and quasicrystalline) having higher cos θ values than the polymers come under the same category with higher cleaning ratings (average rating 2.2 to 3.7). Since many factors such as surface material, temperature, surface defects, and surface roughness influence the contact angle values (for detailed description please refer to paper II), the contact angle measurements can give only sufficient information for grouping the easy-clean polymer materials from the other materials, but in case of other materials, they cannot directly indicate the cleanability of a surface. In addition to surface wettability with oil many other factors such as roughness and surface defects play an important role in determining their cleanability.

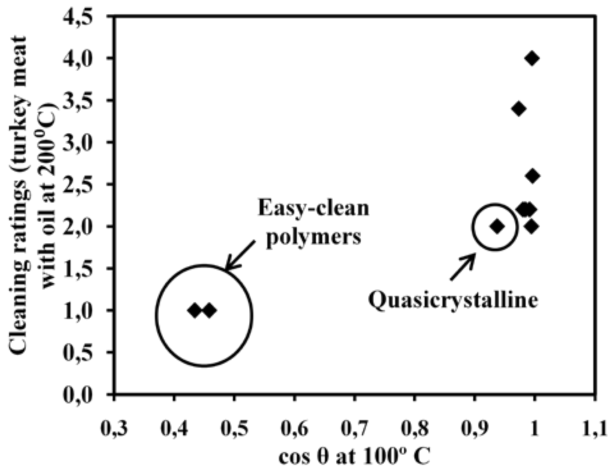


Figure 7.2 Plot of cos θ at 100 °C versus cleaning ratings (turkey meat with oil at 200°C)

When we observe the wettability of the quasicrystalline surface and ceramics coated on EP 316 SS, they show similar behavior with oil at high temperature (200°C). Yet, a distinct difference was observed in the easiness of cleaning the residual oil from these surfaces after the wettability measurements, since the oil adhering to the quasicrystalline surface was more difficult to remove than the oil sticking to ceramics coated on EP 316 SS. This can be explained by the variation in their surface morphologies: In case of the quasicrystalline surface (Figure 3.2i), the surface defects are abundant and thus the oil can easily penetrate into them with a tendency to hide or interlock within the defects from where the oil is difficult to remove afterwards. But in case of ceramics coated on EP 316 SS, there are no such defects (Figures 3.2d, 3.2f & 3.2h) where the oil can go through and hence, the residual oil can be effortlessly removed from them. This once again emphasizes the importance of considering the surface features in addition to surface wettability when cleanability is of concern.

CHAPTER 8

CONCLUSION AND FUTURE PERSPECTIVES

In our studies of different surface materials for contact frying processes, specific surfaces were selected and tested for their non-stick and cleaning properties. The selected surfaces varied in their chemical nature (metal, polymers, ceramics and a quasicrystalline material), surface characteristics (hydrophobic and hydrophilic) and topography (rough and smooth). The different surfaces investigated include 316 grade stainless steel (reference), aluminium (Al Mg 5754), PTFE (Teflon®), silicone, quasicrystalline (Al, Fe, Cr) and three high temperature resistant ceramic coatings: zirconium oxide (ZrO_2), zirconium nitride (ZrN), and titanium aluminium nitride (TiAlN) with two different levels of roughness.

The study of non-stick and cleaning properties of different surfaces was made feasible by the construction of the frying rig which enabled a controlled fouling of different surfaces on steel and aluminium substrates under realistic frying experiments. The non-stick and cleaning experiments of different surfaces were tested on the frying rig as well as in a household convective oven; the results demonstrated that it is not realistic to test non-stick properties for contact frying processes by using a convective oven, as seems to be an established practice in the industry.

In accordance with industry standards pancake was selected as the food model for the frying experiments for initial testing of the non-stick properties of different surfaces. Various methods were developed and tested for evaluating the adhesiveness of different surfaces to the pancake tested. The pancake was much larger in the first experiments (50g versus 10g) and the texture analyzer was used to measure the force to pull the pancake from the frying surface; but, this method failed due to lack of reproducibility. In another test method, a special experimental set-up was used to measure the adhesiveness. The adhesiveness measurements between the pancake and the cable (stainless steel and Teflon® coated stainless steel) using the set-up were able to differentiate between different materials; however, the mode of failure observed in these experiments was mainly cohesive in nature since the pancake adhered to the cable cannot be removed completely instead it was removed in small chunks leaving deposits on the cable. The different methods developed and tested, as explained above, does not seem to be helpful; we therefore developed a subjective evaluation method for testing the non-stick properties of different surfaces.

In the subjective evaluation procedure, the adhesion between the pancake and the frying surface was rated by a standardized procedure. In order to validate the subjective assessment by means of an objective method, the force of adhesion between the pancake and the frying surface was directly measured using a steel scraper. The peak force values measured as the force of adhesion between the pancake and different surfaces using the steel scraper was able to discriminate between the non-stick properties of different surfaces. The release ratings obtained by the subjective method were found to be in good agreement with the peak force values measured by the objective method. The release ratings as well as the peak force values were significantly influenced by the variations in surface material and its topography. A significant effect of the surface topography was demonstrated in our results since all three ceramics gave significantly lower ratings (between one and two grades lower) and lower peak forces when deposited on unpolished steel compared with electro-polished steel.

The different failure modes emerged between the pancake and the ceramic surfaces was based on their difference in the surface topography. The interfacial contact between the pancake and the frying surface was lower for a rough surface than for a smooth surface; thus, a rough surface resulted in significantly less sticking than a smooth (electro-polished) surface. This signifies the importance of surface topography concerns when designing process equipments for semi-solid based foods.

Contact frying experiments with other model foods, i.e. turkey meat, carrots and sweet potatoes at different temperatures with and without the use of oil were carried out on different surfaces in order to examine their cleaning properties. The different surfaces were subjected to a typical cleaning procedure followed in the food industry; the surfaces were cleaned by a combination of chemical (use of cleaning agents) and mechanical cleaning (manual scrubbing). The cleaning ratings were assigned for different surfaces based on a procedure developed and standardized by us; the higher the cleaning rating, the more difficult it is to clean. The use of frying oil gave higher cleaning ratings for the surfaces tested, in particular at high temperatures.

The use of scanning electron microscopy (SEM) for inspecting the cleaned surfaces after the frying process gave informative results regarding the type of residues remaining on different frying surfaces. The difference in elemental composition between stained and unstained spots, which were visible in SEM micrographs of different frying surfaces, was determined using energy dispersive spectroscopy (EDS). A residual film attached to the stainless steel surface was clearly identified from their SEM micrographs; analysis of the residual film detected several non-metallic elements (P, K, Na) with C and P as the most abundant. Such non-metallic elements were also detected in the surface asperities and surface defects of the quasicrystalline material. On ceramic surfaces, elements such as P, K and Na could not be detected; but carbon residues were identified in some of the grain boundaries. The results revealed the inertness of ceramic materials towards their interaction with the food constituents during the frying process. The cleaning properties of different surfaces were affected by their surface topography; in the case of most of the surfaces, surface defects, grooves and scratches contained residues which are likely to result from thermal decomposition of the food. The significance of mechanical interlocking phenomenon on the cleanability issues was clearly demonstrated from our results.

The contact angle measurements were performed with oil on different surfaces at high temperatures. The contact angle of oil measured on different surfaces decreased with an increase in temperature, evidently implying that the adhesion between oil and different surfaces also increased with an increase in temperature. The measured cos θ values were plotted against the cleaning ratings for different surfaces; it was possible to group the easy-clean polymer materials from the other materials using the measured contact angle values. However, in case of other materials (metal, ceramics and quasicrystalline), there is no direct relation between contact angle and cleanability.

The abrasive wear experiments performed to determine the mass loss of different surfaces subjected to different double strokes of the abrasive wheel revealed that the ceramic coatings demonstrated a higher wear resistance than the other materials tested. Among the different ceramics analyzed, titanium aluminium nitride possessed the best wear resistance properties and zirconium nitride, the second best. The zirconium oxide (ZrO_2) ceramic showed poor wear resistance properties similar to that of the polymers since the thin coating layer (0.6µm) could not resist the abrasion experiments and the stainless steel substrate was already revealed after 50 double strokes of the abrasive wheel.

The outcome of the different experiments carried out in the project together revealed many indications in relation to the non-stick and cleaning properties of contact frying surfaces. When pancake was chosen as the food model, the ceramics deposited on electro-polished stainless steel performed poorly in the easy-release tests. When the same surfaces were investigated using other model foods in the frying experiments, i.e. turkey meat, carrots and sweet potatoes, the order in which the different surfaces performed was changed. For example, ceramics coated on unpolished stainless steel performed poorly in the easy-clean tests when tested with turkey meat and frying oil at high temperatures, in contrast to the good performance observed when pancake was used as a model. In both cases, surface topography played a vital role. Contact area effects were responsible for the easy-release properties of the surfaces when pancake was the food model, while mechanical interlocking played an important role in determining the cleaning properties of the same surfaces when other food models were used. This illustrates the complexity of the fouling mechanism in contact frying.

The property of a good frying surface is related to its wetting properties with oil; the surface which possesses good wettability with oil is recommended for the frying process. It is, however, demonstrated from our results that the use of oil for the frying process results in a significantly poorer cleanability of the frying surface. Therefore, whenever new materials are selected for contact frying equipments, one should be aware of the fact that the material which is good for frying purposes may not necessarily be good for easy clean purposes too.

The frying rig developed in our work can offer more practical test conditions for testing the non-stick and cleaning properties of surfaces used for contact frying processes. The subjective evaluation procedure, a less time-consuming and an easy-to-reproduce method, developed in our studies can be used for initial screening of the non-stick properties of different surfaces. The frying and the subsequent cleaning experiments, developed to simulate the practical conditions, can be a suitable procedure for preliminary testing of the cleaning properties of new surface materials before they are installed and used in real factory situations.

Our study demonstrated that several factors, based on the food (type and chemical composition) to be fried and the frying surface in contact (surface chemistry and topography), together contribute to the adhesion and fouling problems during contact frying. The analysis of different factors associated with non-stick and cleaning properties exemplify the complexity of the fouling mechanism in contact frying. The results indicate the need for more advanced methods if one needs to study the influence of different surface materials on the fried product quality. The scientific understanding of the above mentioned issues related to adhesion and fouling can constitute an improved basis for selecting and testing new surfaces for contact frying processes.

In the present work, cost issues were not acknowledged in detail. The costs are, however, dropping by utilizing advanced techniques like PVD for coating purposes.

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APPENDIX – I

SOL-GEL COATINGS

This appendix summarizes the procedures and main results from the work with sol-gel coatings. This approach was eventually abandoned, as explained in Chapter 3. Although the results are negative, they should be reported as part of the thesis.

1. Experimental procedure

1.1 Substrate preparation

The substrates used were 70 x 50 mm plates of 304 SS. The substrates were first ultrasonically degreased with acetone and ultrasonically cleaned in an alkaline solution of pH 11.9 containing 10% Tickopur TR13 solution, for 15 min at 60 º C. The substrates were finally washed with water and air-dried.

1.2. Sol-gel coating solution

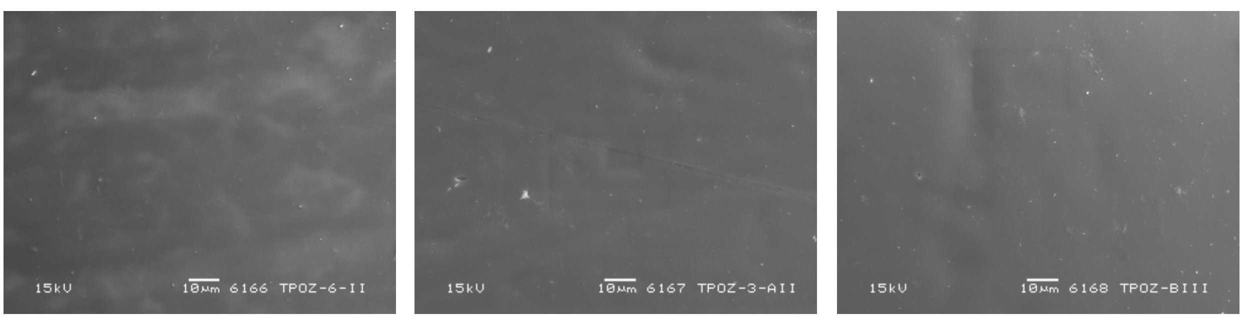
The procedure for preparation of the sol-gel coating solution has been reported in the literature (Zheludkevich, 2004). The silane solution was prepared by mixing 3-Glycidoxypropyltrimethoxy silane (GPTMS) (Alfa Aesar GmbH & Co KG, Karlsruhe), tetraethylorthosilicate (TEOS) (Aldrich Chemical Co., Inc.) and isopropanol in different ratios as shown in Table 1. 1 ml of 68% nitric acid was added as a catalyst for the hydrolysis reaction. The solution was stirred for 30 min at room temperature. The zirconium solution was prepared by mixing ethylacetoacetate (Merck Schuchardt OHG) and tetra-n-propoxyzirconium (TPOZ), 70% in n-propanol (Aldrich Chemical Co., Inc.) in different ratios such as 1:1 and 2:3. Ethylacetoacetate was used as an inhibitor to avoid the rapid hydrolysis of TPOZ. The zirconium solution was stirred for different periods of times at different temperatures as shown in Table 1. The final solution was made by mixing the first and second solution in ratios: 1:3.2 and 1:4 and stirred at room temperature for 60 min and aged for 60 min. The different type of coating procedures is given in the Table 1. The coatings were made by the dip-coating method (Bierwagen, 1995). The substrates were dipped in the final solution and withdrawn at a speed of 36.5 cm/min; the speed was controlled by the dip-coating machine. The coated substrates were then dried in oven at 200 ^{0} C for one hour.

Table 1. Sol-gel coating compositions

Coating Method	Solution	Ratio of Mixing	Temperature (^oC)	Stirring Time (min)	Aging Time (min)
1	Silane	01:04:05	Room	30	-
	Zirconium	01:01	55	120	-
	Final	01:04	Room	60	60
2	Silane	01:04:05	Room	30	-
	Zirconium	01:01	80	60	-
	Final	01:04	Room	60	60
3	Silane	01:01:02	Room	30	-
	Zirconium	02:03	80	60	-
	Final	01:03	Room	60	60

2. Morphology and composition of the films

The morphology of the coatings was analyzed with JEOL JSM 5700 SEM. The coatings were mounted on a stage and sputter-coated with carbon to make them conductive for analysis in SEM. An accelerating voltage of 15 kV was used for all SEM examinations. The SEM photographs shown in Fig. 1 indicate that the morphology of the sol-gel coatings was smooth, flat, crack-free, non-porous and homogeneous.



(a) (b) (c)

Figure 1. Morphology of sol-gel coatings produced by (a) coating method 1 (b) coating method 2 (c) coating method 3

Table 2. Chemical composition of the coatings as determined by energy dispersive spectroscopy

Coating	Zr	Si	O	Cr	Fe
1	45.56	28.73	23.50	0.60	1.61
2	45.67	29.64	21.74	1.28	1.67
3	42.72	28.38	22.07	1.65	5.18

The composition of the different coatings as shown in Table 2 shows that zirconium and silicon were present as main constituents in the coating. The detection of oxygen on the surface indicates that a thin oxide layer could have been present on the surface of the coating. The small amounts of chromium and iron detected in the coating could have been resulting from the substrate's chemical composition (Fe, Ni and Cr).

1. Measurement of adhesion between the coating and the substrate by tape-test

The adhesion measurement was carried out in accordance with the standard ASTM D 3359-02. In accordance with the standard, two types of test methods are possible (i) test method A (ii) test method B. Test method B was selected for the analysis since it is more suitable for laboratory tests. In the test method B, a lattice pattern was made in the coating with eleven cuts in each direction and a pressure sensitive tape was applied over the lattice and detached. Adhesion was assessed by comparison with descriptions and illustrations mentioned in the standard ASTM D 3359-02.

A sharp knife was used to make a lattice pattern with eleven cuts where the cuts were placed 1 mm apart from each other and the additional number of cuts were made at 90^o to the previous cuts. The detached material was removed by wiping with a soft tissue. Then, the pressure sensitive tape was applied over the lattice and removed at an angle of 180^o. The coated substrate was then rated for adhesion in the scale of 0 - 5 which are described as follows:

5: The edges of the cuts are completely smooth; none of the squares of the lattice is detached

4: Small flakes of the coating are detached at intersections; less than 5% of the area is affected

3: Small flakes of the coating are detached along edges and at intersections of cuts; the area affected is 5-15% of the lattice

2: The coating has flaked along the edges and on parts of the squares; the area affected is 15-35% of the lattice

1: The coating has flaked along the edges of cuts in large ribbons and whole squares have detached; the area affected is 35-65% of the lattice

0: Flaking and detachment worse than grade 1

The adhesion was tested at three different areas in the coating and the reported values shown in Table 3 are the mean of three repetitions.

Table 3. Adhesion rating for different sol-gel coatings

Coating Procedure	Adhesion rating (three repetitions)		
	Mean	Minimum	Maximum
1	1.33	1	2
2	1.67	1	2
3	0.67	0	1

The results indicate that the adhesion between the coating and the substrate was very poor resulting in low adhesion ratings. In order to evaluate or test the coating for its non-stick performance, an adequate adhesion is expected between the coating and the substrate. It is likely that the coating could detach form the substrate when it is subjected to frying experiments at high temperature. Hence, these coatings were not tested further to analyze their non-stick or cleaning properties.

Evaluating the Non-Stick Properties of Different Surface Materials for Contact Frying

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Abstract

The paper describes, characterises and validates the construction of an experimental rig for making contact frying experiments under controlled conditions. The construction enables a controlled fouling of different coatings on steel and aluminium plate under realistic frying conditions, in order to evaluate non-stick and cleaning properties of the coatings. In accordance with industry standards pancake was selected as the food model for the frying experiments. The non-stick properties of different frying surfaces (stainless steel, aluminium, PTFE (polytetrafluoroethylene) and three ceramic coatings with two different levels of smoothness) at different temperatures were rated by a standardized rating procedure. The subjective rating assessment was validated by measuring the force of adhesion. A distinct difference was observed in the non-stick properties of the surfaces when they were tested in an oven and on the frying rig. The performances of the surfaces were reproducible and significantly different to be used for screening of new surface coatings for contact frying. Type of coating, surface roughness and temperature each exerted a distinct effect and contributes to a more fundamental understanding of the adhesion mechanisms during contact frying.

Keywords: Contact frying; Fouling; Non-stick properties; Frying surfaces

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1. Introduction

Contact frying is the frying of food by heat transferred through direct contact with a hot surface, usually of steel, cast iron or aluminium. It is exemplified in household scale by pan frying. Contact frying on brat pans or on continuous frying bands is widely applied in the food industry, because it is a desirable process for meeting the increasing demand for industrial ready-made food products of high culinary and nutritional quality. The alternative to contact frying in large scale is deep-fat frying, which has its drawbacks by adding significant amounts of low-quality fat to the products and by the risk of toxic compound formation (Bouchon 2009).

Like most other types of heat processing of food contact frying results in the build-up of a fouling layer on the surfaces in contact with the food. In the case of frying the fouling occurs as a gradual formation of burnt deposits which are more or less firmly bound to the metal surface. This is a side-effect of heat induced reactions among the major food components, such as Maillard reactions, caramelisation and polymerisation of unsaturated fatty acids, where in particular the Maillard reactions are the main pathway to achieve the attractive flavour and colour of a properly made frying crust (DeMan 1999; Therdthai & Zhou 2003; Gogus et al. 2000). Thus, pan frying of pork at a high contact temperature at 250^{o}C gave a more intense flavour of fried meat than frying at 150^{o}C (Meinert et al. 2007). In general, contact frying must be carried out at a relatively high temperature, typically above 200^{o}C, in order to achieve the optimal sensory quality; this is well-known in the art of cooking. However, the high temperature also accelerates the formation of burnt deposits.

To reduce the adhesion of burnt deposits and make cleaning easier the frying surface may be coated or modified in other ways. The ubiquitous coating with PTFE (polytetrafluoroethylene, also known as Teflon®) largely prevents the problems of attached, burnt deposits because of the high bonding energy in the C-F bond, which results in an inert surface chemistry (Balasubramanian & Puri 2009; Zhang et al. 2009). PTFE coating and other organic polymers are not optimal for use in industrial contact frying equipment, because these coatings have poor heat conductivity, do not tolerate continuous exposure to high temperatures enough to give the right product quality, and the surfaces wear easily calling for regular service of the equipment. There is therefore a distinct need for new surface material solutions to improve product quality, reduce down-time for cleaning and reduce maintenance costs.

The search for new surface solutions in food process equipment and development of methods for evaluating the performance of these surfaces are hitherto mainly directed towards applications in systems where the fouling occurs in the liquid phase and at temperatures below 150^{o}C. The fouling occurring inside heat exchangers used for heat processing of fluid foods like milk is a prime example, which has been extensively studied for many years with a view of reducing the rate of fouling and making cleaning more efficient (Changani et al. 1997). This focus of research is reflected in the way the fouling is made experimentally, where the fouling layer typically is deposited at temperatures below or around 100^{o}C (Liu et al. 2006; Saikhwan et al. 2006; Rosmaninho et al. 2007; Mauermann et al. 2009). Such fouling layers evidently do not represent the fouling occurring in contact frying processes with surface temperatures typically at 150-250^{o}C and sometimes above. Even the baking of tomato paste in an oven at 100^{o}C for 1-1.5 h, which is one typical fouling method (Liu et al. 2006; Saikhwan et al. 2006), cannot be expected to result in a fouling layer which is comparable in composition and adhesive properties to that obtained by contact frying of meat, vegetables or batters. Consequently, in the search for improved surface solutions for contact frying the depositing of the fouling layer for testing the surface material should be made under reproducible conditions which are representative of typical frying processes.

In the case of hindering fouling or removing a food material already deposited on the surface of process equipment, there are two types of forces to be considered: (i) cohesive (ii) adhesive. Cohesive force exists between the molecules of the deposit and adhesive force between the deposit and the surface. Thus, the removal of the deposit from the surface can occur as a result of adhesive or cohesive failure or a combination of both (Liu et al. 2006). Cohesive failure occurs when the adhesive force is higher than the cohesive force and adhesive failure occurs when there is a failure of the bond between the deposit and the surface (Hoseney and Smewing, 1999; Kilcast and Roberts, 1997). The nature of the deposit and the surface together determines if the failure mode turns out to be adhesive or cohesive. Earlier studies show that different failure modes can be observed in different foods (Liu et al. 2006) and that modifying the surface properties resulted in reduced adhesion between the deposit and the surface (Saikhwan et al., 2006). Bohnet and Forster (1999) point out that surface topology should also be taken into account since it influences the force of adhesion on the surface.

Apparently, systematic studies of the fouling and non-stick properties of surfaces used in contact frying processes are sparse and are mainly found in patents describing household cookware with modified surfaces having better abrasion resistance than the conventional PTFE coating (Faulkner 2001; Groll 2002; Hayakawa 2007). The methods used in these cases for evaluating the surface properties with respect to adhesion of the food during the heating process (usually called non-stick properties) and the subsequent cleaning are practice-oriented: household frying pans are surface-modified according to the inventions described, and the pans are used to cook or fry different model food products in a standard procedure using a commercial household stove. However, this method of fouling is difficult to reproduce from laboratory to laboratory, because frying on a household stove using a household pan does not give sufficient control over surface temperature and heat flux. In addition, it is costly and impractical to modify the surface of a complete frying pan, and initial testing of smaller specimens of coated metal surfaces would be preferable. The common practice in the industry is to test the non-stick properties of different surfaces by baking in a convective oven, usually using a standardised pancake batter as model.

In the above-mentioned investigations the adhesion of the food after frying is evaluated subjectively using a descriptive scale for giving grades (Haering 2000; Faulkner 2001; Groll 2002; Hayakawa 2007). Human assessments of complex properties, such as texture and flavour of foods or in this case non-stick properties, are acknowledged and commonly applied in food science and technology (Dhaliwal & Macritchie, 1990; Fenn et al. 1994).

In this paper, we will describe, characterise and validate the construction of an experimental rig for making contact frying experiments under controlled conditions. The rig is used for evaluating the non-stick properties of different surface coatings reported to have good non-stick properties, and the results are used in this paper to elucidate and explain the effect of surface roughness. In accordance with industry standards, pancake is selected as the food model for the frying experiments. The non-stick properties of different test coatings are evaluated subjectively using a standardized rating procedure; the subjective assessment is validated by means of an objective method for measuring the force of adhesion. The efficiency of using an oven to demonstrate the non-stick properties of surfaces for contact frying processes, as it is common practice in industry, is also examined.

Although the primary aim of the construction is to establish controlled conditions for fouling of different coatings on steel and aluminium plates under realistic frying conditions, the rig has a wider potential use in the study of the mechanisms governing heat and mass transfer in foods during contact frying or contact baking, since it offers reproducible and controllable experimental conditions.

2. Materials and methods

2.1. The frying rig

The frying rig was constructed in our department workshop, and its principal components are shown in Figure 1. It is a box-shaped construction with a heating surface made of a 300 x 300 x 25 mm aluminium slab cast in the alloy AA-6082 (AlMgSi1). This alloy is corrosion resistant and has a high thermal conductivity in the range of 150-190 $Wm^{-1}K^{-1}$. A PT100, class B temperature sensing resistor in a flexible stainless steel sheath (IEC60751, Labfacility, UK) is inserted into a hole drilled into the centre of the aluminium slab. The aluminium slab rests on a 3 kW thermostated hot-plate, 300 x 300 mm (KR433-U12, Svend Nielsen A/S, DK). A temperature display with an integrated proportional–integral–derivative controller (PID controller) is placed in a box next to the frying table together with a relay, which communicates with the temperature sensor. This set-up allows the centre temperature in the aluminium slab to be controlled within +/- 1^{o}C from a given set point in the range of 100^{o}C to 300^{o}C. The rig is insulated on the sides and bottom by Fiberfrax Duraboard MD, 50mm (Unifrax, UK). The insulation is covered by a stainless steel 304 thin-plate box for protection. The slit between the aluminium slab and the insulated box is sealed with silicone rubber. The frying rig as a whole weighs about 30 kilograms. The entire frying rig is placed on a balance (Signum 1, Sartorius, VWR, DK) having a maximum capacity of 35 kg and an accuracy of 0.1 g. Mass data can be continuously imported into a computer.

The surface temperature of the aluminium slab will be lower than the set temperature because of the upward heat flux to the surroundings. The large mass and high conductivity of the aluminium slab should ensure a uniform surface temperature distribution and give a damping effect on sudden small disturbances in the local heat flux. Surface temperature distribution was validated by temperature measurements using a contact thermometer (SELVISE T200, Jules Richard Instruments, Argenteuil, France) at 16 x 16 points regularly positioned in a rectangular array on the surface of the aluminium slab. The innermost 12 x 12 points defined the central area (about 56 mm from the edge of the slab or above twice its thickness) where the heat flux could be considered uniform and vertical, and the remaining outer area of 2 point’s width on all four sides defined the rim of the slab, where convection from the colder surroundings might influence the surface temperature. The contact thermometer was calibrated against boiling water and ice slurry before the experiments. The frying rig was set to 200^{o}C and after 30 minutes the surface temperature of the aluminium slab were measured at the 256 points.

2.2. Food model

Pancake was selected as the food model for the frying experiments. It is a suitable model because it sticks to the frying surface, it is easy to reproduce, and it is widely used in the industry for testing non-stick properties of surfaces, also at Accoat A/S, Denmark, where one of us is working as an industrial Ph.D.-student. A pancake batter of suitable viscosity was developed from trial and error experiments. Pasteurized egg white (50 g), pasteurized egg yolk (30 g), milk (150 g), wheat flour (125 g), and sugar (20 g) were mixed using a household egg beater. The water content of the pancake batter was measured by drying for 24 h at 105^{o}C (Nielsen 1994) and found to be 1.46 kg H_2O /kg dry matter = 59.3 w/w% water.

2.3. Frying tests

Before using the rig it was thermally equilibrated to the set temperature for 30 minutes. A stainless steel or aluminium disc with or without coating (see section 2.4) was placed centrally on the aluminium slab. To ensure good thermal contact, heat-resistant copper paste (OKS Antiseize Copperpaste #240, Højstrup Industrilim, DK) was applied to the bottom of the frying disc using a paint brush before the disc was placed on the frying rig. The disc was left for 10 minutes to achieve thermal equilibrium; this was controlled by reading the surface temperature once per minute with the contact thermometer. The food model, in this case 10.0 g pancake batter, was poured onto the hot surface. The pancake was fried for 600 seconds on one side. Mass loss because of evaporation was monitored continuously by recording the weight every second. The mass was found to decrease approximately linearly in the range of 100 to 500 s. Mass loss rate was calculated in this region by linear regression, and the mass loss in gram was calculated by multiplying the slope [g/s] with 400 s. After frying, the pancake was removed from the surface using a metal spatula. For each type of coating, frying experiments were carried out at two different set temperatures, 160 and 200^{o}C, with five repetitions for each temperature. After cleaning the frying discs were re-used for the next experiment.

2.4. Frying surfaces

All the frying discs were circular plates cut by water-jet cutting in stainless steel or aluminium with a diameter of 90 mm and a thickness of 5 mm. This thickness was chosen empirically as a compromise between the tendency to deform due to thermal stresses when the cold pancake batter was poured onto the hot disc and the need to keep the thickness as small as possible because of the rather low heat conductivity of stainless steel 13.4 $Wm^{-1}K^{-1}$ (Gebhart, 1993).

The different frying surfaces investigated include aluminium (Al Mg 5754), 316 grade stainless steel, PTFE (Teflon®) and three high temperature resistant ceramic coatings: zirconium oxide (ZrO_2), zirconium nitride (ZrN), and titanium aluminium nitride (TiAlN). These particular ceramic coatings were chosen for the purpose since they were widely quoted in patents describing non-stick coatings for cookware (Faulkner 2001; Groll 2002; Ge 2005).

PTFE was spray coated on the Al Mg 5754 aluminium discs and provided by Accoat A/S, Kvistgard, Denmark. The ceramic coatings were manufactured by Physical Vapour Deposition technique (PVD) (Mattox 1998) and provided by Technological Institute, Aarhus, Denmark. They were all deposited on two different stainless steel discs with two different levels of roughness: Unpolished stainless steel (UP 316 SS) and electro-polished stainless steel (EP 316 SS). Roughness (R_a) of the ceramic coatings was measured using a Surftest SJ-201 Surface Roughness Tester (Mitutoyo, USA) according to Japanese Standards Association JIS B0601-1982 (Stylus speed = 0.25 mm/s, stylus force = 4 mN). R_a was ca. 0.7 µm for the coatings on UP 316 SS and 0.3-0.5 µm for the coatings on EP 316 SS. Coating thickness was measured on samples cut perpendicular to the coating using Scanning Electron Microscopy (SEM) at DTU Centre for Electron Nanoscopy. The ceramic coating thicknesses were 0.6 µm for ZrO_2, 6 µm for ZrN and 5-6 µm for TiAlN.

2.5. Release tests

The ease with which the pancake can be removed from the frying disc was evaluated subjectively, adopting the rating procedures described in the patent literature (Faulkner 2001; Groll 2002; Hayakawa 2007). The following numerical ratings were used, see also Figure 2:

1 - Pancake is removed easily without any stains left on the surface. The force of adhesion is negligible.

2 - Pancake is removed without any damage but with concentric frying patterns left on the surface. The force of adhesion is felt to be small.

3 - Pancake is removed without any damage but with moisture or small brown stains left on the surface. The force of adhesion is felt to be noticeable.

4 - Pancake is removed without any appreciable damage, but pancake dough stains are left on the surface. This means that the force of adhesion is close to the force needed to overcome the force of cohesion.

5 - Pancake is damaged during removal, and broken pancake bits are sticking to the surface. The force of adhesion is at certain spots higher than the force of cohesion.

The release ratings are interpreted so that surfaces with a rating of 1 have excellent non-stick properties, surfaces with a rating of 2 to 3 have good non-stick properties and those with a rating of 4 to 5 have poor non-stick properties.

2.6. Oven tests

The pancake tests were also carried out in a household convection-oven (Lytzen, Herlev, Denmark) at the same temperatures, 160 and 200^{o}C as in the frying experiments. Five repetitions were made for each temperature. 10 g of pancake batter was poured onto different surfaces coated on rectangular stainless steel plates of dimension 70 x 50 mm with a thickness of 1 mm and baked in the oven for 600 s at the selected temperature. The non-stick properties of the coated plates were evaluated as described in section 2.5.

2.7. Force of Adhesion

The aim of developing this method is to validate the subjective assessment by means of an objective method. Earlier studies indicate that it is possible to measure the force required to remove food deposits from different surfaces (Liu et al. 2002; Liu et al. 2006). In the present method, the force required for the removal of a test pancake from different frying surfaces is measured using the test apparatus constructed at Accoat A/S and sketched in Figure 3. The pancake was pulled by a rectangular steel scraper, 50 x 31 mm, which moves at a constant speed of 150 mm/sec on a linear guide steel rail (model LWH Kugleføringer, Acton A/S, Vallensbæk Strand, Denmark) of dimension 210 x 12 mm by means of a ball-type cage. The steel rail is attached under an aluminium bridge, 260 x 80 mm, which is fixed tightly on the frying surface by means of two clampers. The scraper is attached to the material testing instrument (model LR 5K, Andertech Plastteknik A/S, Humlebæk, Denmark) by means of a nylon string normally used in the friction studies, and the corresponding force versus distance curve was recorded by a material test and data analysis software (NEXYGEN^{TM} Plus, Lloyd Instruments, West Sussex, UK) of the testing instrument. The distance between lower edge of the scraper and the frying surface was 0.6 mm. The peak force was recorded as a measure of adhesiveness (Johnson 1996). In these tests the mass of the pancake was reduced to 2 g to ensure that the diameter of the pancake (25 mm) was smaller than the scraper width (31 mm). For each type of coating, frying experiments were carried out at two different set temperatures, 160 and 200^{o}C, with three repetitions for each temperature.

2.8. Statistical analyses

Standard statistical analyses (analysis of variance – ANOVA and Student's t-test) were used throughout. Both tests are rather robust towards smaller deviations from the normal distribution (Montgomery 2009). The release ratings are discrete values and they only approximately follow a normal distribution in the closed range of 1 to 5; therefore, conclusions on *differences* in the rating values were based on a significance level of $P<0.001$. Measurements of force of adhesion were tested on the basis of a significance level of $P<0.01$. These more strict demands on probability level were chosen to reduce the risk of a Type I error in screening experiments. Reproducibility of the experiments was tested on the basis of a significance level of $P<0.05$ in all cases.

3. Results and discussion

3.1. Surface temperature distribution of the aluminium slab

The average surface temperature of the central area (144 points) was 190.8^{o}C (standard deviation = 0.9^{o}C) and of the rim 189.7^{o}C (standard deviation = 1.3^{o}C). The difference of ca. 9^{o}C between the set point (200^{o}C) and the central average surface temperature arises from the combined effect of the gradient through the slab and in particular from the steady-state heat loss from the surface. The low standard deviation of the measurements in the central area demonstrated that the heat flux was highly uniform. A t-test showed that the difference between the two average temperatures, although small (1.1^{o}C) was statistically significant ($t = 7.07$, $P < 0.001$). This indicates that convective influx of cold air plays a detectible, but also in practice minimal effect on the heat flux outside the central area.

Differences in the convective heat loss from day-to-day variations in the environment will cause the surface temperature to vary slightly (1-2^{o}C). When an aluminium frying disc was placed on the slab and allowed to equilibrate for 10 minutes it was observed that slab temperature in the vicinity of the disc increased slightly (about 2^{o}C) due to the local lowering of the heat flux (the disc has a minute insulating effect). The temperature of the disc (average of 10 measurements) was on the average 1.4^{o}C lower than the slab temperature near the disc, when no copper paste was used, see also section 3.2.

3.2. Effect of copper paste

To test the effect of applying copper paste at the bottom side of the frying discs, a series of experiments with aluminium plates (ten with and ten without copper paste) were made at 160^{o}C and 200^{o}C, respectively, and the surface temperatures recorded. The results are shown in Table 1. There is a statistical significant rise in the surface temperature of the frying discs by the use of copper paste ($P<0.001$) and the standard deviations are smaller. This demonstrates that the copper paste has the desired effect of improving thermal contact. However, the data also indicate that even without using copper paste, the variation in surface temperature is small, and the thermal resistance between the discs and the slab is low. Since copper paste is messy and difficult to remove from the surfaces, the paste may be omitted in future experiments.

3.3. Mass loss profile

The pancake mass difference measurements on various surfaces at two different temperatures are shown in Table 2. An ANOVA shows that there is no significant difference in the mass loss profile for tests using different plates at the same temperature ($F = 1.50$; d.f. = 8, 68; $P > 0.05$). This demonstrates that the tests are reproducible and also that different thermal conductivities of the plates (e.g. aluminium versus stainless steel) do not play a significant role for the rate of evaporation, which means that the heat and mass transfer from the frying surface to the pancake and the rate of evaporation is determined by the pancake itself. This is a reasonable conclusion since the pancake dough is viscous and soon solidifies, so that water transport to the surface is controlled by diffusion. At the upper surface of the pancake temperature must be around 100^{o}C or less, as long as evaporation takes place. As expected, the set temperature has a profound effect on the rate of evaporation by creating a steeper temperature gradient from bottom to top of the pancake ($F = 32.5$; d. f. = 1, 68; $P < 0.001$).

3. 4. The frying rig versus the oven

Table 3 shows the results of the release tests for the different surfaces tested on the frying rig. As the only material, PTFE obtained a rating of one in all cases, both on the frying rig and in the oven, demonstrating the unique non-stick properties of PTFE. The uniform results for PTFE evidently mean that they should be excluded from the subsequent ANOVAs, where the effects of the different surfaces and temperatures are evaluated.

For the other materials the difference between the results obtained in the oven and on the frying rig is striking: All surfaces (except PTFE) tested in the oven obtained a rating of five at all temperatures, while testing on the frying rig showed a much better and varied performance for the same surfaces. For example, aluminium gave poorer performance than stainless steel in the release tests, which is in accordance with practical experience using household pans for pancake baking. This indicates that the frying rig offers more realistic test conditions for discriminating between different surfaces than the convection oven. There is, indeed, a distinct difference between the heating mechanism that takes place in an oven and the frying table. In an oven, the pancake is heated and dried from above by the forced convective heat transfer from the circulating hot air in the oven, but in contact frying the pancake is heated from below, while evaporation takes place from above under conditions of natural convection.

3.5. Release rating and peak force

The release ratings and the peak force values for different surfaces at two different temperatures are shown in Table 3. The data are plotted against each other in figure 4. For the data points below 8 N there is a good linear correlation between peak force and release rating (R^2=0.92). The figure also shows that for peak forces above 8 N the pancake sticks so firmly to the surface that it disintegrates, given a rating of 4 to 5. The outlying three data points at peak forces above 8 N all stem from tests at 200^{o}C on ceramics deposited on electro-polished steel, and the all exhibited cohesive failure. These results taken together suggest that the peak force has a good correlation with the release rating as long as the failure is adhesive between the pancake and the surface.

In all force of adhesion measurements testing the PTFE coating, the pancake did not stick at all to the surface but easily slided off resulting in a peak force value of zero. This implies that the results for PTFE should be excluded from the subsequent ANOVAs.

3.6. Effect of surface material and temperature

Even a quick glance on Table 3 shows that both temperature and surface material would give a statistical significant effect on the peak force values (For temperature $F = 103$; d.f. = 1, 30; $P < 0.001$; for surface material $F = 43$; d.f. = 7, 30; $P < 0.001$; reproducibility and interaction between the two factors is not significant). Therefore, it is more informative to compare and contrast the differences between particular surfaces separately rather than altogether.

First, stainless steel and aluminium are compared with each other since they are regularly used in the household kitchen. Stainless steel performs better than aluminium because it gave significantly lower release ratings ($F = 15.38$; d. f. = 1, 12; $P < 0.01$) as well as lower peak force values ($F = 13.08$; d. f. = 1, 6; $P < 0.05$) compared to those of aluminium. This observation is in agreement with Kaushik and Bala (2010) who stated that stainless steel is non-reactive and easy-to-clean when compared to that of aluminium.

The different ceramic materials were then compared to each other. It appears that the type of ceramic material composition i.e., TiAlN, ZrN or ZrO_2 does not have a significant effect on the peak force values at 160^{o}C; however, a small difference can be noticed between the peak force values of TiAlN and ZrO_2 at 200^{o}C ($t = 3.04$; d. f. = 4; $P < 0.05$). An explanation for this could be that these ceramic nitrides and the stainless steel oxidize when they come into contact with air (Faulkner, 2001), and these protective oxide layers are likely to behave similar in their sticking behaviour with pancake at 160 and 200^{o}C.

It is of great interest to know if any of the ceramic materials performs better than stainless steel. Therefore, each of the ceramic surfaces coated on unpolished steel was compared individually with stainless steel by t-tests. It was found that their peak force values at 160^{o}C and 200^{o}C were not significantly different; these results were in agreement with data from the release tests shown in Table 3. These results show that the non-stick performance of these ceramics does not seem to be superior to that of stainless steel. However, the ceramics are more resistant to wear compared to steel (Budinski, 2004).

As mentioned above, the release rating and the peak force for different surfaces increases significantly with temperature, cf. Table 3. This is hardly surprising since an increase in temperature accelerates the chemical reactions: caramelization, maillard browning reaction and protein denaturation which are responsible for forming the adhesive bonding between the pancake and the frying surface.

3.7. Effect of surface topography

It is clear from Table 3 that there is a significant effect of the surface topography since all three ceramics gave significantly lower ratings (between one and two grades lower) and lower peak forces when deposited on unpolished steel compared with electro-polished steel. The ANOVAs in Table 4 show that there is a significant effect of surface topography on the release ratings and peak forces. When the pancake is fried on ceramics deposited on unpolished steel, the failure is adhesive since the pancake can be completely removed from the substrate. When the pancake is fried on ceramics deposited on electro-polished steel, a partial removal of the pancake with broken pancake bits sticking to the surface was clearly observed, specifying that a cohesive failure occurs within the pancake. This clear effect of roughness can be explained as follows: On a rough surface, the real area of contact is much smaller than the geometrical area due to surface asperities (Bhushan et al., 2003) and hence the interfacial contact between the pancake dough and a rough surface will occur at discrete points. This results in a weak adhesion between pancake and the rough surface leading to an adhesive failure manifested by lower release ratings and peak forces than when cohesive failure occurs. An electro-polished smooth surface possesses higher contact area than a rough surface and thus a more complete interfacial contact is obtained between the pancake dough and the smooth surface. This results in a stronger force of adhesion leading to a cohesive failure, which is manifested in relatively higher release ratings and peak forces.

4. Conclusion and perspectives

The frying rig described in this paper has a number of distinctive advances for testing different surfaces for their non-stick properties in contact frying processes. Tests can be done on small specimens of the materials, in the present case by using 90 × 5 mm discs of stainless steel or aluminium as substrates for depositing the experimental surface coatings. The thermal contact between the discs and the hot surface is good, even when thermal paste is omitted. The validation of the rig shows that the heat flux is uniform over the entire central area of the aluminium slab which constitutes the hot surface. The effect on surface temperature arising from local disturbances and day-to-day variations in the heat flux are small, typically about 2^{o}C, and thus negligible when comparing with the span of relevant set temperatures (in this case 160^{o}C and 200^{o}C). The data on mass loss during the baking process shows that the baking process itself is reproducible and that differences in the thermal conductivity of the plates can be ignored when comparing tests done at the same set temperature. The good reproducibility of the experiments performed on the frying rig can be exploited with advantage in more rigorous quantitative studies of the heat and mass transfer in contact frying processes, and we are pursuing this in an ongoing parallel study. Thus, the frying rig presented and validated here has a wider potential of use as an experimental set-up in food engineering.

The subjective way of evaluating non-stick properties, a test which is found to be less time-consuming and rather easy to reproduce, is appropriate for screening different surfaces, since a good non-stick surface is apparently characterized by ratings which are below 3 and the rating was reproducible with a low standard deviation (around 0.3 units on a 1-5 integer scale). The peak force values generated by the force of adhesion experiments were able to discriminate between different surfaces at different temperatures. The release ratings obtained by the subjective method were found to be in good agreement with the peak force values measured by the objective method. The release ratings as well as the peak force values were significantly influenced by the variations in surface material, temperature and surface topography; contact area effects based on surface topography was found to be a principal factor in determining the failure to be adhesive or cohesive.

The work has demonstrated that pancake itself is a good model to test the non-stick properties of different surfaces. However, it is also demonstrated that it is not realistic to test non-stick properties for contact frying processes by using a convective oven, as seems to be an established practice in industry. The tests gave a release rating of five in all cases, except PTFE, and the oven test was unable to discriminate between the surfaces and temperatures applied. This reflects that a test performed in a convection oven is just a test of non-stick properties in a convective oven, and the results cannot be extrapolated to contact frying, where the mechanism of heat and mass transfer in the food is different.

In a parallel study we have investigated the same surfaces using other model foods in frying experiments, i.e. turkey meat, carrots and sweet potatoes (Ashokkumar et al., 2010); these foods do not stick to the frying surfaces but instead leave residues, which means that it is cleaning properties rather than non-stick properties of the frying surfaces which is the important performance indicator. Evaluation of different surfaces for contact frying therefore involves more than testing for non-stick properties. Nevertheless, the information obtained from using the pancake model to test for non-stick properties is useful for reaching a deeper understanding of the factors contributing to the search for better frying surfaces.

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Figures and Tables

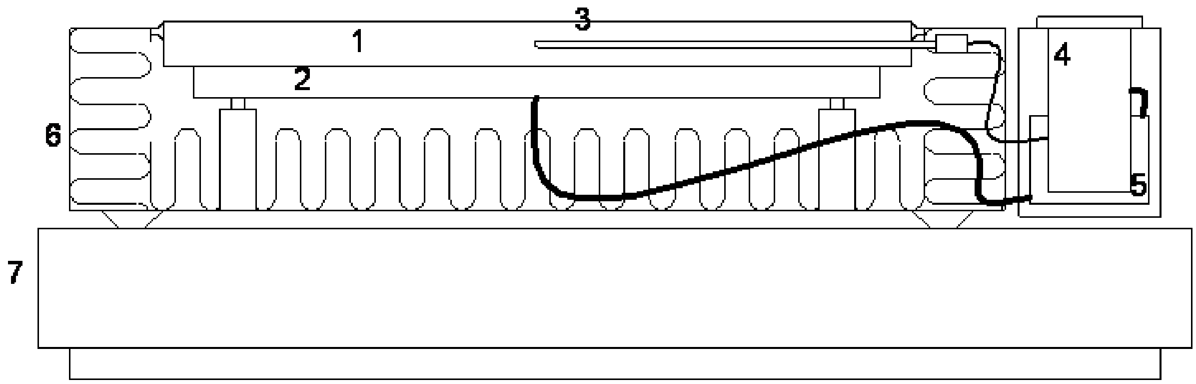

Figure 1. Principal components in the frying table: 1. Aluminium Plate 2. Heating Plate 3. PT100 sensor 4. Temperature Display 5. Relay 6. Insulated box 7. Balance Plate

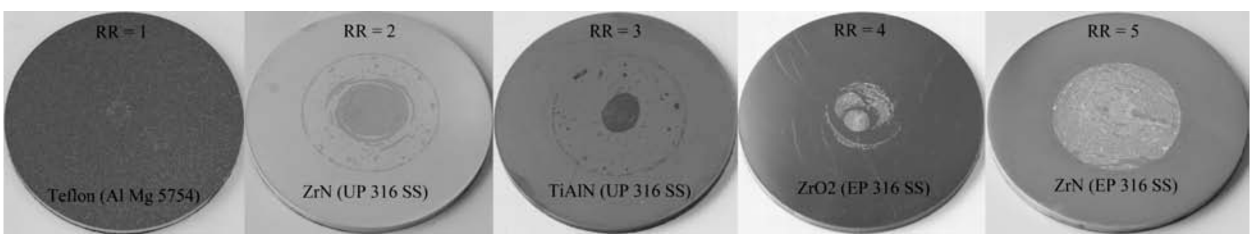

Figure 2. Photographs depicting various types of stains, that can be seen after frying pancake on different surfaces at different temperatures, according to which the release ratings have been given (RR : Release Rating)

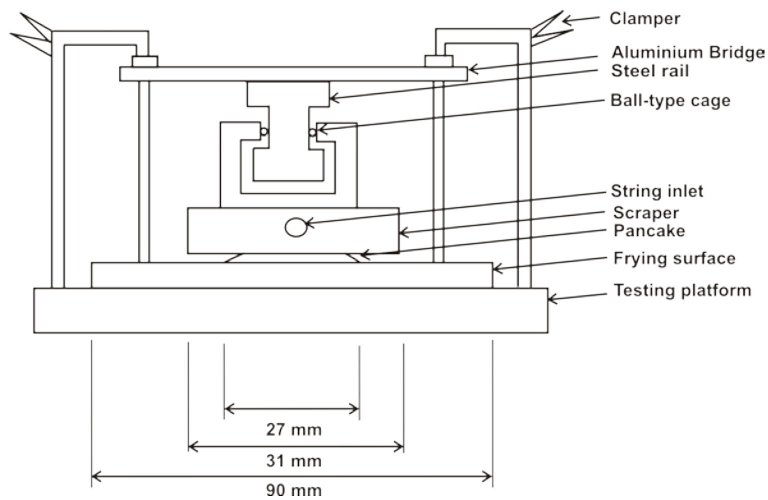

Figure 3. Schematic view of the apparatus employed to measure the force of adhesion

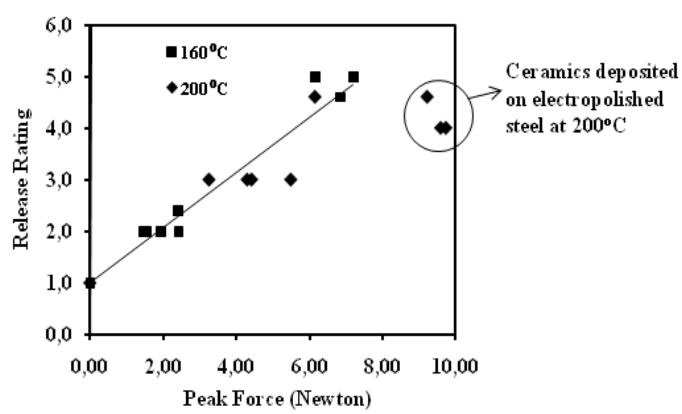

Figure 4. Plot of peak force (in Newton) versus release rating

Table 1 - Temperature measurements on ten different aluminium surfaces with and without the use of copper paste at 160°C and 200°C

Set temperature (°C)	Use of copper paste	Mean surface temperature (°C)	SD[a] (°C)	t-value calculated
160	Yes	154.2	0.09	9.79 (P<0.001)
	No	152.0	0.20	
200	Yes	192.6	0.08	4.15 (P<0.001)
	No	191.2	0.32	

a - Standard Deviation

Table 2 - Mean values of mass loss from pancake baking experiments

Temperature / Material	Mean mass difference in g over 100 – 500 s	
	160 °C	200 °C
Teflon (Al Mg 5754)[a]	0.94	1.34
Aluminium Al Mg 5754	1.16	1.38
316 Stainless Steel	0.81	1.51
TiAlN (UP 316 SS)[b]	1.05	1.22
TiAlN (EP 316 SS)[c]	1.02	1.30
ZrN (UP 316 SS)[d]	0.79	1.33
ZrN (EP 316 SS)[e]	0.99	1.31
ZrO_2 (UP 316 SS)[f]	1.08	1.28
ZrO_2 (EP 316 SS)[g]	1.14	1.31

Standard deviation on the means (five repetitions) : 0.11 g

a - Teflon coated on Al Mg 5754 aluminium plate

b - TiAlN coated on unpolished 316 stainless steel plate

c - TiAlN coated on electropolished 316 stainless steel plate

d - ZrN coated on unpolished 316 stainless steel plate

e - ZrN coated on electropolished 316 stainless steel plate

f - ZrO_2 coated on unpolished 316 stainless steel plate

g - ZrO_2 coated on electropolished 316 stainless steel plate

Table 3. Mean values of peak force and release ratings at different temperatures

Temperature / Material	Set temperature (° C)	Mean peak force in Newton (three repetitions)	Mean release ratings (five repetitions)
Teflon (Al Mg 5754)[a]	160	0.0	1.0
	200	0.0	1.0
Aluminium Al Mg 5754	160	2.4	2.4
	200	6.1	4.6
316 Stainless Steel	160	1.9	2.0
	200	4.3	3.0
TiAlN (UP 316 SS)[b]	160	1.5	2.0
	200	3.3	3.0
TiAlN (EP 316 SS)[c]	160	6.9	4.6
	200	9.2	4.6
ZrN (UP 316 SS)[d]	160	1.7	2.0
	200	4.4	3.0
ZrN (EP 316 SS)[e]	160	6.2	5.0
	200	9.7	4.0
ZrO_2 (UP 316 SS)[f]	160	2.4	2.0
	200	5.5	3.0
ZrO_2 (EP 316 SS)[g]	160	7.2	5.0
	200	9.6	4.0

Standard deviation on the means of peak force (three repetitions) : 0.42 Newton
Standard deviation on the means of release ratings (five repetitions) : 0.17
a - Teflon coated on Al Mg 5754 aluminium plate
b - TiAlN coated on unpolished 316 stainless steel plate
c - TiAlN coated on electropolished 316 stainless steel plate
d - ZrN coated on unpolished 316 stainless steel plate
e - ZrN coated on electropolished 316 stainless steel plate
f - ZrO_2 coated on unpolished 316 stainless steel plate
g - ZrO_2 coated on electropolished 316 stainless steel plate

Table 4. Calculated F-values from ANOVAs to analyze the effect of roughness on data from Table 3

Method	Set temperature (° C)	Factor	F	Degrees of freedom	Significance
Release rating	160	Ceramic Surfaces	1.00	4, 20	P > 0.05
		Roughness	462	1, 20	P < 0.001
		Interaction	1.00	2, 20	P > 0.05
		Reproducibility	1.00	4, 20	P > 0.05
	200	Ceramic Surfaces	6.00	4, 20	P < 0.05
		Roughness	216	1, 20	P < 0.001
		Interaction	6.00	2, 20	P < 0.05
		Reproducibility	1.00	4, 20	P > 0.05
Force of Adhesion	160	Ceramic Surfaces	3.56	2, 10	P > 0.05
		Roughness	253	1, 10	P < 0.001
		Interaction	0.29	2, 10	P > 0.05
		Reproducibility	0.80	2, 10	P > 0.05
	200	Ceramic Surfaces	1.43	2, 10	P > 0.05
		Roughness	64	1, 10	P < 0.001
		Interaction	0.73	2, 10	P > 0.05
		Reproducibility	0.50	2, 10	P > 0.05

Technical University of Denmark ***Research and Innovation, PhD programme***

January 2010

Joint author statement

If a thesis contains articles made in collaboration with other researchers, a joint author statement about the PhD-student's part of the article shall be made by each of the co-authors, cf. article 12, section 4 of the Ministerial Order No. 18 February 2008 about the PhD degree

Title of the article:	Evaluating the Non-Stick Properties of Different Surface Materials for Contact Frying		
Author(s):	Saranya Ashokkumar, Jens Adler-Nissen		
Journal:	Journal of Food Engineering		
PhD-student:	Saranya Ashokkumar	CPR-no.:	201185-3326
Signature of the PhD-student:		Date:	8 December 2010
Co-author:	Jens Adler-Nissen	Signature:	

Description of each author's contribution to the above-mentioned article:

Saranya Ashokkumar, as a first author, carried out the experimental work and have written the full manuscript. Jens Adler-Nissen as a co-author reviewed the full manuscript and gave comments and suggestions on the manuscript.

Factors Affecting the Wettability of Different Surface Materials with Vegetable Oil at High Temperatures and its Relation to Cleanability

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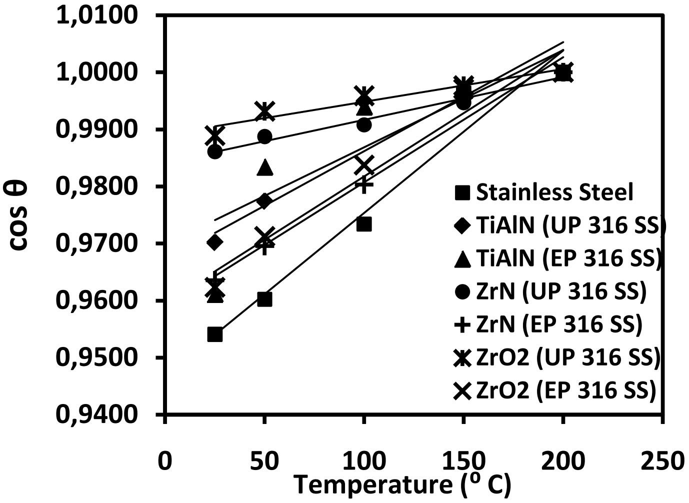
Abstract

The main aim of the work was to investigate the wettability of different surface materials with vegetable oil (olive oil) over the temperature range of 25 - 200^{o}C to understand the differences in cleanability of different surfaces at high temperatures. The different surface materials investigated include stainless steel (reference), PTFE (polytetrafluoroethylene), silicone, quasicrystalline (Al, Fe, Cr) and ceramic coatings: zirconium oxide (ZrO_2), zirconium nitride (ZrN) and titanium aluminium nitride (TiAlN). The ceramic coatings were deposited on stainless steel with two different levels of roughness. The cosine of the contact angle of olive oil on different surface materials rises linearly with increasing temperature. Among the materials analyzed, polymers (PTFE, silicone) gave the lowest cos θ values. Studies of the effect of roughness and surface flaws on wettability revealed that the cos θ values increases with increasing roughness and surface flaws. Correlation analysis indicates that the measured contact angle values gave useful information for grouping easy-clean polymer materials from the other materials; for the latter group, there is no direct relation between contact angle and cleanability. In addition to surface wettability with oil many other factors such as roughness and surface defects play an essential role in determining their cleanability.

Keywords: *Wettability; Different surface materials; Vegetable Oil; Cleanability; High temperatures; Roughness and surface flaws;*

Graphical Abstract

Plot of cos θ versus temperature for metal and ceramic surfaces where cos θ rises linearly with increase in temperature.



Research Highlights

- Cos θ of olive oil on different surface materials rises linearly with increase in temperature; slopes are much higher for quasicrystalline and polymers than for ceramics
- Increase in surface roughness and surface flaws increases surface wettability
- Contact angle values gave useful information for grouping easy-clean polymer materials from the other materials

Introduction

The contact angle of a liquid drop on a solid surface is an expression of the work of adhesion between the liquid and the solid. Contact angle measurements between water and different surfaces are an established procedure for evaluating the easy-to-clean properties of different surfaces (Kuisma et al. 2007; Maatta et al. 2007; Handojo et al. 2009; Saikhwan et al. 2006; Mauermann et al. 2009; Yoon and Lund, 1994). Kuisma et al. (2007) studied the cleanability of wall tiles using uncoated and fluoropolymer, zirconia and titania coated ceramic glazed surfaces and reported that the fluoropolymer coatings gave the highest contact angle values with water and also the best easy-clean properties. Maatta et al. (2007) compared the cleanabilities of different coated glazed surfaces and reported that the surface chemistry indicated by contact angle measurements affected the cleanability of the surfaces in removing the oil soils rather than removing inorganic and organic particle soils. Handojo et al. (2009) concluded that the contact angle measurements were useful to predict the difficulty in removing various milk-based products from the surface of glasses. In a study by Saikhwan et al. (2006) a strong correlation was found between the contact angle (expressed as the surface energy, see theory) of different surfaces and the adhesive strength of the tomato paste. Mauermann et al. (2009) analyzed the influence of surface modifications with low surface energy materials, by using starch and whey protein deposits and reported that low-energy materials gave less starch deposits when compared to normal stainless steel. However, it seems that contact angle measurements are not always a precise indicator of easy-to-clean properties. Yoon and Lund (1994) found that even though the contact angle values were higher on teflon and polysiloxane surfaces compared to stainless steel, these alternatives to steel did not result in a reduced milk fouling compared to stainless steel.

The work described in the present paper is motivated by a search for new surface materials for industrial food frying equipments. The materials should have easy-release and easy-clean properties, yet also have good surface characteristics for frying. Faulkner (2001) states that “In terms of surface chemistry, a perfect non-stick cookware is one which would be wetted very well by olive oil but it should behave as hydrophobic as possible towards water-based dispersions”. On highly hydrophobic surfaces like PTFE, the oil form discrete droplets at the interface between food and surface which is not desirable for a good frying process (Faulkner, 2001).

In our studies of new surface materials we have been selected classes of materials for our studies that range from hydrophobic to hydrophilic materials (refer to Table 1). The different surface materials investigated include PTFE (polytetrafluoroethylene), silicone, quasicrystalline (Al, Fe,Cr) and ceramic coatings: zirconium oxide (ZrO_2), zirconium nitride (ZrN) and titanium aluminium nitride (TiAlN) with two different levels of smoothness. These materials are known for their good non-stick properties and widely quoted in patents (Faulkner 2001; Groll 2006; Ge 2005) and scientific literature (Balasubramanian & Puri 2009; Minevski et al., 2009; Rivier et al., 1993; Rummel 1984; Zhang et al. 2009). Stainless steel is used as a reference material.

In a previous study, we analyzed the cleanability of the different surfaces by frying three different kinds of foods (carrot, sweet potato, turkey meat) with and without the use of oil at 200 and 240^{o}C; the frying experiments were carried out under controlled conditions using a specially designed frying rig (Ashokkumar et al., 2010). Cleaning ratings were assigned for the different surfaces where low ratings indicate an easy-to-clean surface and vice-versa. When the surfaces were cleaned after the frying process at high temperature, traces of the oil used for frying was found to remain on them, resulting in relatively higher cleaning ratings (Ashokkumar et al., 2010). These observations suggest that studying the interfacial properties of different surfaces could aid in the process of choosing an appropriate easy-to-clean surface.

The spreading behaviour of a liquid on a solid during high-temperature applications will be different from the same at room temperature. Kuznetsov and Martynov (1972) studied the contact angle of lubricating oils on stainless steel surfaces at elevated temperatures (20 - 180^{o}C) and reported that the contact angle decreases with increase in temperature. For high temperature processes like frying, it is relevant to study the interfacial properties at the frying temperature. At high frying temperatures, eventually water evaporates but the oil used for frying cannot evaporate and remain on the frying surface influencing its cleanability.

Very few articles have been published regarding the use of oil for contact angle measurements. Michalski et al. (1998a) studied the adhesion of edible oils to different food contact surfaces like low-density polyethylene, polyethylene terephthalate, stainless steel and glass. They found that the experimental adhesion of oil to different surfaces was correlated to the contact angle measurements with oil at 20^{o}C on those surfaces. It was reported by Michalski et al., (1998a) that oils were chosen for their studies since they are particularly difficult to remove from surfaces and hence create important cleaning problems. This suggests that if the frying surface has good wetting properties with oil, difficulties may arise in cleaning the surfaces after the frying process. The main of this study is therefore to study the relation between wettability and cleanability of different surfaces at high temperatures.

The oil used for the contact angle experiments at high temperatures is not likely to degrade since the measurements were taken within a short lapse of time (10-15 seconds). Rossi et al., 2009, in their studies, used four different vegetable oils for frying potato strips for 12 hours; the fried oil sample was taken once in every three hours and the contact angle of the fried oil was measured at room temperature. They found out that the contact angle of the oil varied very little, although the oil was used before in a frying process for 12 hours. The oil degradation fact will therefore be disregarded in these experiments; the study of the influence of different factors on wettability will be based on the factors associated with different surfaces.

The wettability is governed by both the chemical nature of the liquid and that of the surface, including its roughness (Mafu et al. 1990; Silva et al. 1995). Many studies concluded that the roughness of a surface exerts an influence on the surface wettability (Prabhu et al., 2009; Chen and Duh, 2000; Sun et al. 2007; Veeramasuneni et al. 1997). A high value of substrate roughness improves substrate wetting by the liquid since higher roughness provides additional surface area in the form of crests and valleys for spreading (Prabhu et al., 2009). Chen and Duh (2000) also explains that the rough surfaces will wet more if reactive energy only is considered since they have more active sites. Sun et al. (2007) indicate that lower roughness value implies a lower surface free energy. The effect of roughness on the wettability has been tested in this work with the contact angle measurements on ceramics with two different levels of roughness.

Theory

The angle formed by the solid-liquid interface and the liquid-vapor interface for a drop of liquid on a horizontal solid surface is called the contact angle (Handojo et al. 2009). The contact angle, θ, is related to the interfacial energies of solid - liquid (γ_{SL}), liquid - vapor (γ_{LV}) and solid - vapor (γ_{SV}) by Young's equation (Bargir et al. 2009; Handojo et al. 2009; Sun et al., 2007):

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos\theta \qquad (1)$$

Rhee et al., 1971 found that the cosine of the contact angle of a liquid metal on a ceramic surface shows a linear increase with increase in temperature in accordance with the equation (2). Fox et al., 1955 found that the cosine of the contact angle of an organic liquid on high energy surfaces also shows a linear increase with increase in temperature.

$$\cos\theta = A + BT\ (^{o}C) \qquad (2)$$

where A is a constant and B is the slope.

The contact angle of a liquid drop on a rough surface follows the Wenzel equation (Veeramasuneni et al., 1997):

$$\cos\theta_a = r\cos\theta \qquad (3)$$

where θ_a - apparent contact angle (measured through a microscope), r - surface roughness ratio(r = a/A = (da/dA $\geq$ 1), a - actual area of surface, A - apparent area or geometrical area of the surface, θ - intrinsic contact angle.

2. Materials and methods

2.1. Materials

Extra-virgin olive oil was used for the contact angle measurements at room temperature and at high temperatures. Extra-virgin olive oil was selected for the purpose, since it was commonly used in other adhesion studies (Michalski et al. 1998a; Michalski et al. 1998b). Both oils were purchased from Netto, a Danish Super Market. Contact angle measurements were also made with rapeseed oil at room temperature to test the influence of oil type on the wettability of different surfaces.

2.1.1. Surfaces

The different surface materials investigated in this study are presented in Table 1.

2.1.1.1. Ceramic Coatings

The three high temperature resistant ceramic coatings: zirconium oxide (ZrO_2), zirconium nitride (ZrN), and titanium aluminium nitride (TiAlN), manufactured by Physical Vapor Deposition (PVD) (Mattox 1998) process, were provided by Technological Institute, Aarhus, Denmark. DC magnetron sputtering is the technique used to deposit the coating. They were all deposited on two different stainless steel discs of 90 mm in diameter with two different levels of roughness: Unpolished stainless steel (UP 316 SS) and electro-polished stainless steel (EP 316 SS). Coating thickness was measured on samples cut perpendicular to the coating using Scanning Electron Microscopy (SEM) at DTU Centre for Electron Nanoscopy. The ceramic coating thicknesses were 0.6 µm for ZrO_2, 6 µm for ZrN and 5-6 µm for TiAlN. An overview of the different surfaces and their modification techniques are given in Table 1.

2.1.1.2. Quasicrystalline Coatings

Quasicrystalline metallic materials are finding wider use due to their good non-stick properties (Rivier et al., 1993; Minevski et al., 2009). The quasicrystalline coating supplied by Saint-Gobain, France was based on $Fe_xCr_yAl_z$ material. The coating was deposited on stainless steel disc (90 mm in diameter) by High-velocity oxy-fuel (HVOF) flame spray method (Shaitura and Enaleeva, 2007; Huttunen-Saarivirta et al., 2003). The thickness of the coating was reported to be 300 ± 25 µm.

2.1.1.3. PTFE (Polytetrafluoroethylene)

Polytetrafluoroethylene is widely known for its unique non-stick properties due to the high bonding energy in the C-F bond, which results in an inert surface chemistry (Balasubramanian & Puri 2009; Zhang et al. 2009). Polytetrafluoroethylene coated on stainless steel disc (90 mm in diameter) was supplied by Whitford Worldwide, Brescia, Italy. The thickness of the coating was reported to be 25 ± 10 µm.

2.1.1.4. Silicone

Silicone coatings are generally used for non-stick baking pans (Rummel 1984). The silicone rubber ELASTOSIL® E 60 is used for making the silicone coating. The silicone was spray coated on anodized Al-Mg 5754 aluminium substrate by Accoat A/S, Kvistgard, Denmark. The aluminium (Al Mg 5754) was anodized in a sulphuric acid bath at room temperature with a voltage of 20 V with a current of 2 A/dm^2 for 20 minutes. The anodized layer thickness is 23 ± 2 µm. The ratio of ELASTOSIL® E 60 and acetone in the coating solution was 1:4. It was sprayed onto the top of the anodized aluminium disc which is 90 mm in diameter. The coated panel was finally cured by oven baking at a temperature of 200^{o}C for 5 minutes with a final coating thickness of 19 ± 2 µm.

2.2. Methods

2.2.1. Cathodic cleaning

Cathodic cleaning (Eurof Davies and Shah, 1960) was performed in order to clean the different surfaces prior to the contact angle measurements. The process was carried out for two minutes by passing a current of 10 amperes through the electrolyte (20 g/l sodium hydroxide solution). After this process, the surface was immersed in a dilute solution of sulphuric acid for a period of 1 - 2 minutes to remove the excess NaOH ions remaining on the surface. The surface was then rinsed with running water and dried using a hair dryer before each measurement. These conditions were standardized and found to be optimal for this experiment. Aluminium can be etched by alkaline electrolyte and therefore the surfaces: silicone (coated on anodized aluminium) and QC (Al, Fe, Cr) were instead cleaned by acetone followed by rinsing with ethanol.

2.2.2. Contact Angle

The contact angle measurements were obtained using the sessile drop method with a dataphysics OCA-20 contact angle analyzer at Danish Polymer Centre, DTU, Denmark. This instrument is equipped with a CCD video camera having a resolution of 752 x 582 pixels which can take 50 pictures per second. The instrument has a temperature controlled chamber ranging between -10 and 400^{o}C with manual or electronic dosing units. The surface was placed in the chamber and heated to the required temperature. A 4 µl drop of olive oil was placed on the surface and the image of the drop is captured immediately. The contact angle with an accuracy of ± 0.1^o is calculated from the drop image by the image analysis software integrated in the system. Each experiment is repeated for five times by placing new drops on different points on the surface and the reported contact angle values are the average of five repetitions. The photographs of olive oil drop on different surfaces at 25°C are shown in Figure 1.

2.2.3. Roughness Measurements

The two-dimensional roughness profile of the different surfaces was measured using a Surftest SJ-201 Surface Roughness Tester (Mitutoyo, USA) according to Japanese Standards Association JIS B0601-1982. The 5 µm diamond stylus traverses on the test material at a speed of 0.25 mm/s. The downward force of the stylus was 4 mN and the measurement range was 350 µm. The cut-off length was 0.8 mm. Before each measurement, the instrument was calibrated using a reference work piece. Roughness (Ra), usually expressed in µm, explains the average height or depth of the peaks above and below the average centerline of a surface (Kuisma et al., 2007). The results were expressed as the mean of ten readings for each material which is shown in Table 1.

2.2.4. Scanning Electron Microscopy

A scanning electron microscope (FEGSEM 200F) was used to study the morphology of the different surfaces. The photomicrographs were taken with a magnification of 10 µm using an accelerating voltage of 10 kV for all the examinations except for PTFE and silicone coatings where 1 kV was employed to obtain photomicrographs with good resolution.

2.2.5. Statistical Analysis

All the contact angle experiments were repeated for five times and the average value is reported as the contact angle. The effect of temperature and surface material on the wettability of different surfaces was analyzed by two-way ANOVA. The effect of type of oil on the wettability was analysed by two-way ANOVA with oil and surface material as two different factors. The effect of surface roughness on the wettability was analysed by two-way ANOVA with surface material and surface roughness as two different factors. Significant differences between the slope values of different surface materials were nalyzed by means of a pairwise t-test with 8 degrees of freedom.

3. Results

3.1. Effect of temperature

The different temperatures employed in this study produce a strong effect on the wettability of different surfaces with olive oil (For temperature $F = 2.1 \times 10^3$; d. f. = 4, 196; $P < 0.001$; for surface material $F = 40.7 \times 10^3$; d. f. = 9, 196; $P < 0.001$; for interaction between the two factors $F = 294$; d. f. = 36, 196; $P < 0.001$; reproducibility is not significant). Figure 2 shows the plots of cos θ versus temperature for different surfaces from which their respective slopes were determined. Our results follow equation (2) since the cosine of the contact angle of vegetable oil on different surfaces shows a linear increase with increase in temperature. This observation is in agreement with previous studies (Fox et al., 1955; Rhee et al., 1971). In order to recognize how fast the wetting behavior of different surfaces changes with temperature, it is essential to compare and contrast the differences between the slopes of the different surfaces. Among the different materials tested, the quasicrystalline material demonstrates a faster increase in cos θ as the temperature is increased and hence it has the highest slope among the different materials. The slope of quasicrystalline material was compared individually with the slope of different materials and its slope is significantly different from stainless steel ($t = 62$; d. f. = 8; $P < 0.001$), ceramics (t value ranges from 64 to 74; d. f. = 8; $P < 0.001$) and PTFE ($t = 15$; d. f. = 8; $P < 0.001$); but, not significantly different from silicone ($t = 1.50$; d. f. = 8; $P < 0.001$).When the slope of stainless steel was compared individually with the slopes of different ceramics, a significant difference was found between them (t value ranges from 17 to 51; d. f. = 8; $P < 0.001$). The polymers (PTFE and silicone) showed a significant difference in their slope values when compared individually with the slopes of stainless steel and ceramics (for PTFE t value ranges from 16 to 22 and for silicone t value ranges from 24 to 29; d. f. = 8; $P < 0.001$). When slopes of the two polymers: PTFE and silicone were compared with each other, they were significantly different ($t = 9.3$; d. f. = 8; $P < 0.001$) and silicone shows higher rate of increase in cos θ as the temperature is increased compared to PTFE. The slope difference between different surfaces stresses that the factors related to the surface, such as chemical nature, surface roughness and surface defects, itself have an important effect in determining the surface wettability when there is a rise in temperature.

3.2. Effect of different surface materials

The different surfaces employed in this study produce a significant effect on their wetting behavior with olive oil at different temperatures (For surface material $F = 40.7 \times 10^3$; d. f. = 9, 196; $P<0.001$; for temperature $F = 2.1 \times 10^3$; d. f. = 4, 196; $P < 0.001$; for interaction between the two factors $F = 294$; d. f. = 36, 196; $P < 0.001$; reproducibility is not significant). The metal, ceramics and the quasicrystalline material showed a significant difference in their wettability with olive oil in the temperature range: 25 - 150^{o}C (For surface material $F = 3.5 \times 10^3$; d. f. = 7, 156; $P < 0.001$; for temperature $F = 3.3 \times 10^3$; d. f. = 4, 156; $P < 0.001$; for interaction between the two factors $F = 8.6 \times 10^2$; d. f. = 28, 156; $P < 0.001$; reproducibility is not significant); but, there is no difference in their wettability at 200^{o}C, since these surfaces were completely wetted by olive oil at 200^{o}C. The polymers (PTFE and silicone) showed a unique trend in the wetting behavior when compared to stainless steel, ceramics or the quasicrystalline material in the whole temperature range 25 - 200^{o}C. The wettability of PTFE and silicone is significantly different from each other (For surface material $F = 102$; d. f. = 1, 36; $P < 0.001$; for temperature $F = 552$; d. f. = 4, 36; $P < 0.001$; for interaction between the two factors $F = 52$; d. f. = 4, 36; $P < 0.001$; reproducibility is not significant). The different surface materials have a strong influence on the wettability at different temperatures as there is a difference in their chemical nature: metal, polymer or ceramic and surface topography.

3.3. Effect of surface roughness

The spreading behavior of oil on different surface materials is influenced by surface roughnesses. The value of roughness parameter, Ra, for ceramics coated on UP 316 SS ranges from 0.67 to 0.72 µm and for ceramics coated on EP 316 SS varies from 0.27 to 0.47 µm. The effect of surface roughness on wettability was tested by comparing cos θ values for the ceramics coated on UP 316 SS and EP 316 SS in the temperature range of 25 - 150^{o}C. The cos θ values, in the temperature range of 25 - 100^{o}C, for the ceramics coated on EP 316 SS are significantly lower than the same coated on UP 316 SS. This shows that an increase in surface roughness results in an increase in the wettability of ceramic materials following the Wenzel's equation (3). Our results are similar to that of Prabhu et al. 2009 who concluded that the contact angle decreased with increase in roughness supporting the Wenzel's proposition. However, at high temperature (150^{o}C) the difference is no longer significant (For roughness $F = 3.9$; d. f. = 1, 20; $P > 0.05$; for surface material $F = 32$; d. f. = 2, 20; $P < 0.001$; for interaction between the two factors $F = 5.1$; d. f. = 2, 20; $P < 0.05$; reproducibility is not significant) and it vanishes completely at 200^{o}C when all surfaces wet completely (contact angle = 0^{o}). The effect of roughness cannot be seen at high temperatures like 150^{o}C and 200^{o}C due to the very low contact angles measured on ceramics at these temperatures. The slope derived from cos θ versus temperature for the ceramics coated on UP 316 SS and EP 316 SS were also compared and they were statistically significant (For roughness $F = 985$; d. f. = 1, 20; $P < 0.001$; for surface material $F = 52$; d. f. = 2, 20; $P < 0.001$; for interaction between the two factors $F = 163$; d. f. = 2, 20; $P < 0.001$; reproducibility is not significant).

3.4. Effect of surface defects

In addition to the roughness factor, any flaws or presence of holes in the surface should also be considered in determining the surface wettability. The morphology of unpolished stainless steel (Figure 3a) and an electro-polished stainless steel substrate (Figure 3b) illustrates a distinct difference between the two surface treatments. The morphology of the ceramics coated on UP 316 SS (Figure 3d, 3f & 3h) illustrates lot of grooves in the surface due to the presence of grain boundaries in its underlying UP 316 SS substrate whereas the morphology of the ceramics coated on EP 316 SS is smooth and dense (Figure 3e, 3g & 3i); since the properties of the film deposited by a physical vapour deposition process are influenced by the morphology of the substrate surface, electro polished smooth substrate (EP 316 SS) yield more dense coatings than a rough substrate (Mattox, 1998). The morphologies suggest that the oil could easily wet the irregular surface grooves or defects of the ceramics coated on UP 316 SS possibly giving rise to mechanical interlocking phenomena, the most widely accepted theory for adhesion between a rough substrate and the adhering material (Allen 1993; Michalski, 1997; Mittal 1977; Nelson, 1995). When the surface gets polished, the defects will be relatively less as well as the chance for interlocking will be reduced in comparison to the rough surfaces; this explains the decrease in cos θ for the polished surfaces.

Among the different surfaces studied, the quasicrystalline surface demonstrated a faster decrease in cos θ values with rise in temperature (see section 3.1) as well as its morphology depicted numerous manufacturing defects which can be apparently seen in figure 3c. The morphology of the quasicrystalline surface suggests that the oil can readily flow through the surface defects increasing its wettability at high temperatures or decreasing the cos θ values faster as the temperature rises.

3.5. Effect of oil type

To investigate the effect of oil type, contact angle measurements were performed with rapeseed and olive oil on UP 316 SS, ZrO_2 (UP 316 SS) and ZrO_2 (EP 316 SS) at 25^oC. The data are shown in Table 3. Data analysis shows that there is a significant effect of surface ($F = 175.2$; d.f. = 2, 20; $P < 0.001$) but there is no effect of oil type ($F = 0.3$; d.f. = 1, 20; $P > 0.05$) on the wettability of different surfaces. Rapeseed and olive oil are similar types of oil which are low in saturated fats and rich in monounsaturated fats and suitable for use in frying processes. The data analysis suggests that the conclusion drawn from the other contact angle measurements using olive oil can be used for rapeseed oil, too.

3.6. Cleaning Ratings

The cleaning ratings for different surfaces after frying with turkey meat at 200^oC are shown in Table 4. These data were taken from Ashokkumar et al. (2010) in which cleaning ratings, from a scale of 1 - 5, were assigned for different surfaces after the frying process where low ratings indicate an easy-to-clean surface and vice-versa. The data analysis by t-test as shown in Table 3 shows that the use of oil for frying has produced a significant effect on cleaning ratings of the surfaces: UP 316 SS, TiAlN (UP 316 SS); but no such effect of oil can be seen on cleaning ratings of the surfaces: TiAlN (EP 316 SS), ZrN (UP 316 SS), ZrN (EP 316 SS), ZrO_2 (UP 316 SS), ZrO_2 (EP 316 SS), QC (Al, Fe, Cr), PTFE and silicone.

4. Discussion

A clear difference can be seen in the wettability of the different surface materials at room temperature. As the temperature rises the difference disappears between the metals, ceramics and quasicrystalline materials except polymers. The quasicrystalline material have a high contact angle with oil at room temperature and thus one could expect it to be a better easy - to - clean surface than the stainless steel and ceramics. But as the temperature rises, it shows a fast decrease in the contact angle and at 200^{o}C it shows a complete wetting with oil similar to the behaviour of stainless steel and ceramics. The cleaning ratings, obtained after frying different foods using oil at different temperatures, for quasicrystalline material and ceramics were also similar. However, the polymers (PTFE, silicone) showed a different trend in the wetting behavior when compared to other materials since even at high temperature (200^{o}C) the polymers maintain a high contact angle (57.1^{o} for PTFE; 56.3^{o} for silicone) with the oil; this observation supports Faulkner's statement that the oil form discrete droplets at the interface between food and PTFE surface. In order to achieve a good adhesion between a liquid and a surface, it is necessary that the liquid should completely wet the surface (Allen, 1993). It is therefore apparent that the poor wetting of polymer surfaces with oil at high temperature generates poor adhesion between the oil and the polymer surfaces during frying eventually resulting in good easy-to-clean properties or lower cleaning ratings (Table 3). The data obtained from our study implies that the surfaces (metal, ceramics and quasicrystalline) are wetted very well by olive oil at high temperatures; but, good wettability also enhances the adhesion between oil and the surfaces, decreasing their cleanability. Hence, correlation analysis was carried out to investigate whether any direct relation exists between the cos θ values and cleaning ratings for the different surfaces which will be described in the following paragraph.

The cleaning ratings for different surfaces were assigned once the frying experiments were performed at 200^{o}C. In frying, the heating medium often reaches temperatures of 180 - 200^{o}C but the temperature on the food surface in contact with the frying surface is lower because the food is cooled by moisture evaporation (Claeys et al. 2005). Therefore, the temperature of the frying oil will be less than the actual frying temperature; the oil temperature in the present work is probably between 100 and 150^{o}C. A correlation analysis was carried out by plotting the cleaning ratings for different surfaces versus their cos θ values at 100 and 150^{o}C. A definite correlation could not be obtained between the cleaning ratings and cos θ values at both temperatures. But an association can be seen based on the nature of the material: Polymers possess lower cos θ values at high temperatures and gave lower cleaning ratings (average rating 1.1 - 1.2). Other surfaces (metal, ceramics and quasicrystalline) having higher cos θ values than the polymers comes under the same category with higher cleaning ratings (average rating 2.2 - 3.7). Contact angle measurements can therefore give information necessary for grouping the materials but they cannot directly indicate the cleanability of a surface; in addition to surface wettability with oil many other factors such as roughness and surface defects play an important role in determining their cleanability.

When we observe the wettability of quasicrystalline surface and ceramics coated on EP 316 SS they show similar behavior with oil at high temperature (200^{o}C). Yet, a distinct difference was observed in the easiness of cleaning the residual oil from these surfaces after the wettability measurements; the oil adhering to quasicrystalline surface was more difficult to remove than the oil sticking to ceramics coated on EP 316 SS. This can be explained based on the variation in their surface morphologies: In case of quasicrystalline surface (Figure 3c), the surface defects are abundant and thus the oil can easily penetrate into them with a tendency to hide or interlock within the defects from where the oil is difficult to remove afterwards. But in case of ceramics coated on EP 316 SS, there are no such defects (Figure 3e, 3g & 3i) where the oil can go through and hence, the residual oil can be effortlessly removed from them. This once again emphasizes the importance of considering the surface features in addition to surface wettability while cleanability is concerned.

Conclusion

The work has demonstrated that temperature significantly influences the wettability of different surface materials; the cosine of the contact angle of olive oil on different surface materials rises linearly with increasing temperature. A range of surface materials studied indicate that the polymers retain a high contact angle with oil even at high temperature (200^{o}C) whereas the other materials show complete wetting with oil at 200^{o}C. The investigation of the effect of roughness on wettability reveals that the surface wettability increases when roughness increases; however the roughness effect becomes insignificant at high temperature (150^{o}C) and it disappears completely at 200^{o}C when all surfaces wet completely. The higher cos θ values for ceramics coated on unpolished steel, in comparison to the same coated on polished smooth steel, imply that their uneven surface flaws can be easily wetted by oil leading to automatic interlocking between oil and the flaws.

These results together suggest that the contact angle measurements can be utilized as a preliminary technique to recognize the wetting properties of different food contact surfaces. Surfaces varying in their chemical nature, surface roughness and surface defects can be characterized since the contact angle values measured on different surfaces were found to be influenced by these surface attributes. Contact angle measurements, especially those performed with oil are of special interest with regard to selection of a good frying surface since surface possessing good wetting properties with oil is desired for a frying process. It should also be perceived that such surfaces showing good wettability with oil gave rise to cleanability issues. In such cases, contact angle measurements can be used to classify different materials with respect to cleanability. Nevertheless, contact angle measurements cannot directly estimate the cleanability of a surface since factors related to the surface itself play an important role in determining the cleanability.

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Figures and Tables

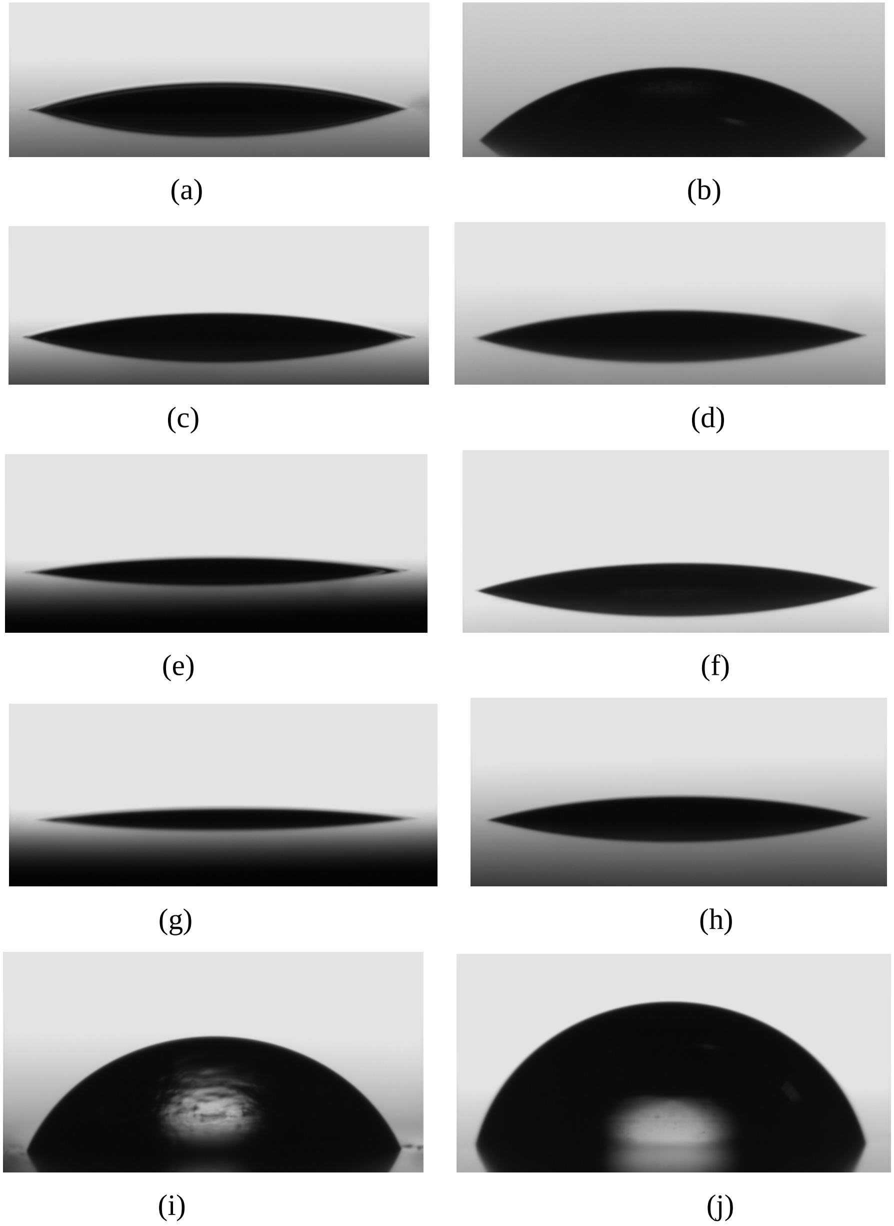
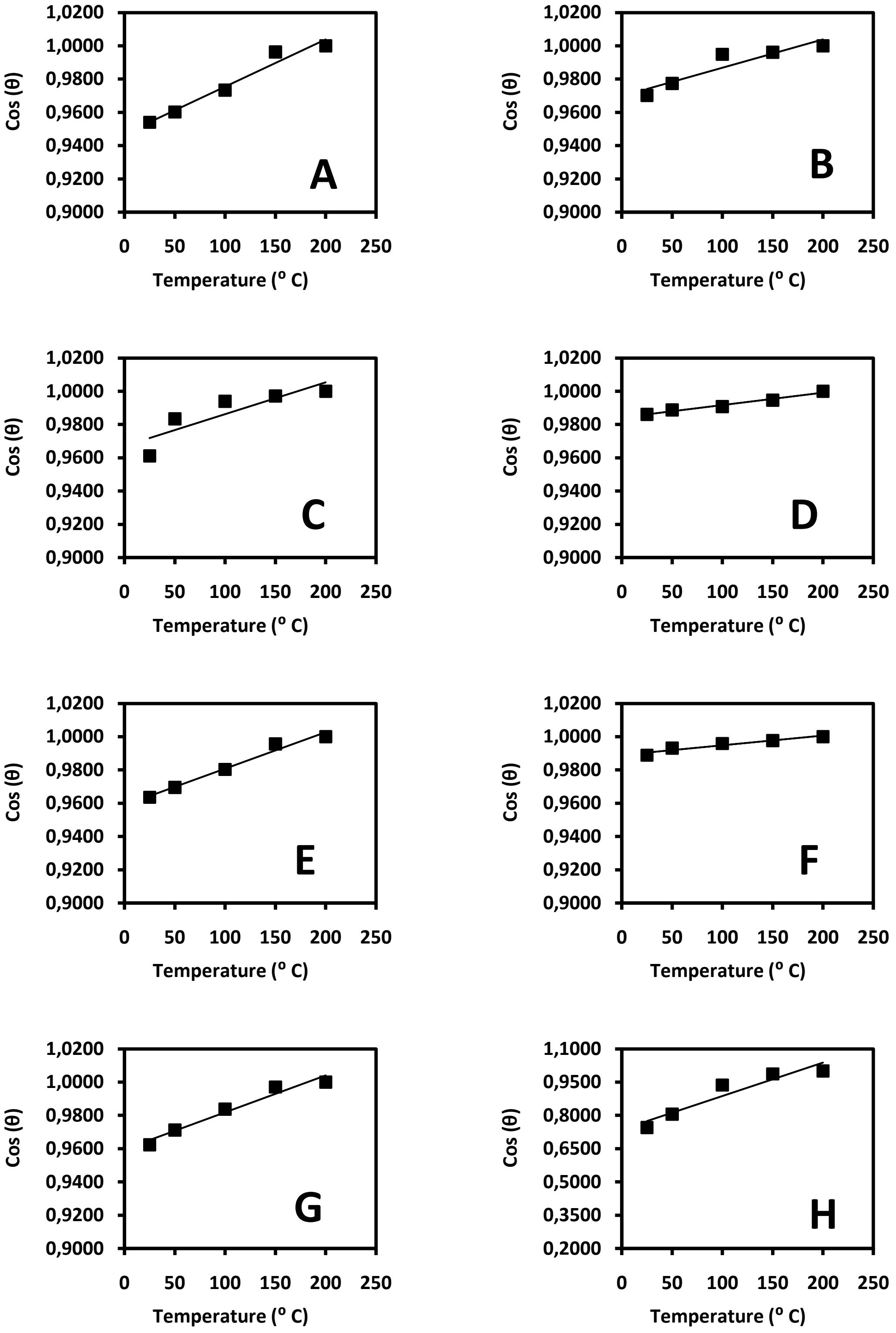


Figure 1. Photographs of olive oil drop on different surfaces at 25 ^{o} C (a) UP 316 SS (b) QC (Al, Fe, Cr) (c) TiAlN (UP 316 SS) (d) TiAlN (EP 316 SS) (e) ZrN (UP 316 SS) (f) ZrN (EP 316 SS) (g) ZrO_2 (UP 316 SS) (h) ZrO_2 (EP 316 SS) (i) PTFE (j) Silicone.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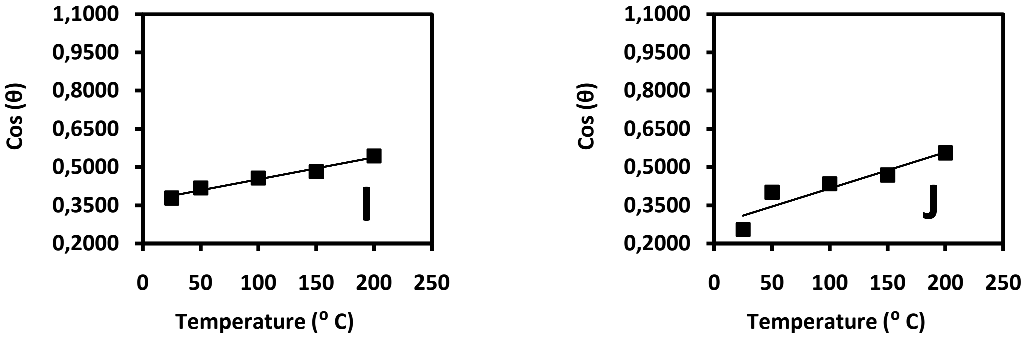

Figure 2. Plot of cos θ versus temperature for different surfaces (A) UP 316 SS (B) TiAlN (UP 316 SS) (C) TiAlN (EP 316 SS) (D) ZrN (UP 316 SS) (E) ZrN (EP 316 SS) (F) ZrO_2 (UP 316 SS) (G) ZrO_2 (EP 316 SS) (H) QC (Al, Fe, Cr) (I) PTFE (J) Silicone. (Note: Scales for QC (Al, Fe, Cr), PTFE and silicone are different from that of other materials).

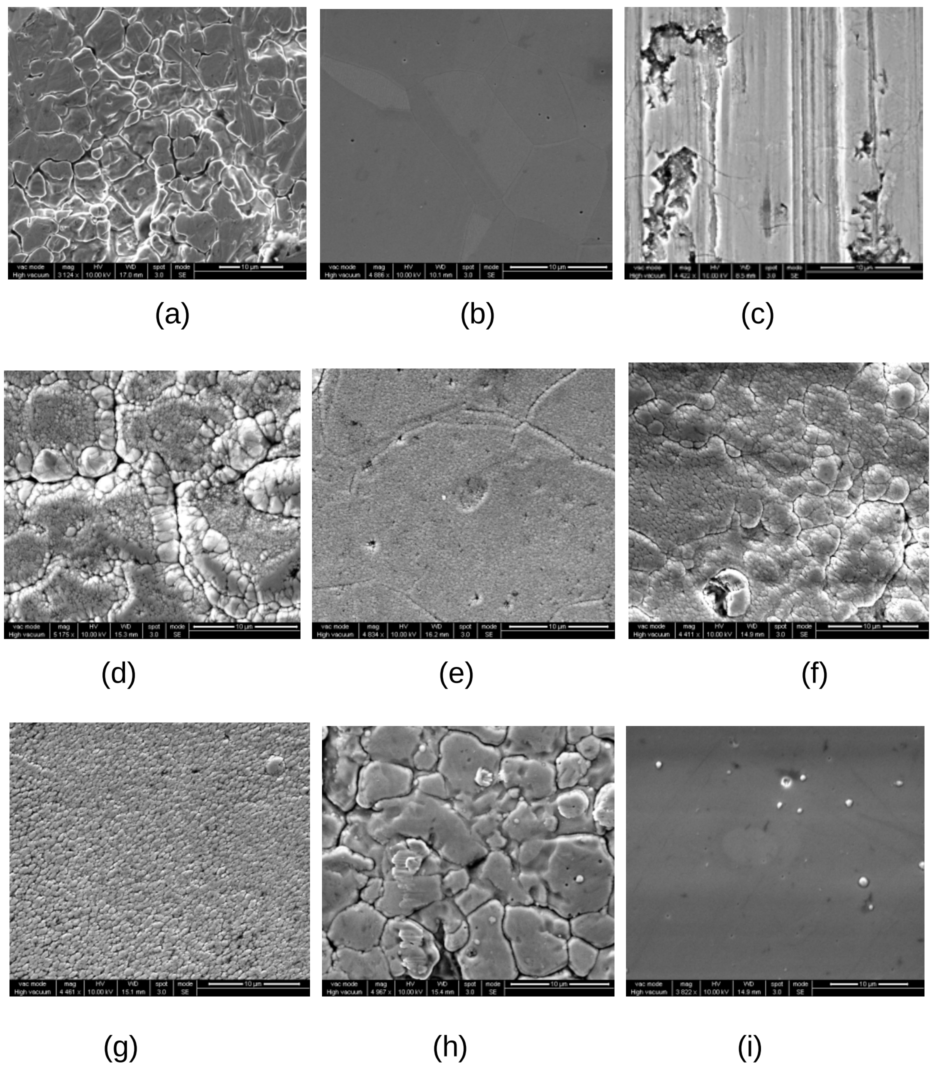

Figure 3. SEM photomicrographs of surfaces with different morphologies (a) UP 316 SS substrate (b) EP 316 SS substrate (c) QC (Al, Fe, Cr) (d) TiAlN (UP 316 SS) (e) TiAlN (EP 316 SS) (f) ZrN (UP 316 SS) (g) ZrN (EP 316 SS) (h) ZrO_2 (UP 316 SS) (i) ZrO_2 (EP 316 SS)

Table 1. The surface code, surface description, coating method, roughness (R_a) and water contact angle values of the different surface materials

Surface Code	Description	Coating method	Roughness Value Ra (μm)	Water Contact Angle (^{o})
UP 316 SS	Unpolished 316 Stainless steel	None	0.44 ± 0.04	57.7 ± 0.4
TiAlN (UP 316 SS)	Titanium Aluminium Nitride coated on UP 316 SS[a]	Physical Vapour Deposition	0.72 ± 0.08	54.4 ± 0.2
TiAlN (EP 316 SS)	Titanium Aluminium Nitride coated on EP 316 SS[b]	Physical Vapour Deposition	0.47 ± 0.06	48.5 ± 0.6
ZrN (UP 316 SS)	Zirconium Nitride coated on UP 316 SS[a]	Physical Vapour Deposition	0.68 ± 0.08	54.7 ± 0.8
ZrN (EP 316 SS)	Zirconium Nitride coated on EP 316 SS[b]	Physical Vapour Deposition	0.27± 0.04	41.9 ± 1.1
ZrO_2 (UP 316 SS)	Zirconium Oxide coated on UP 316 SS[a]	Physical Vapour Deposition	0.67 ± 0.08	65.2 ± 0.7
ZrO_2 (EP 316 SS)	Zirconium Oxide coated on EP 316 SS[b]	Physical Vapour Deposition	0.4 ± 0.06	56.1 ± 0.3
QC (Al, Fe, Cr)	Quasicrystalline coated on UP 316 SS[a]	High Velocity Oxy-Fuel	0.3 ± 0.07	108.3 ± 0.5
PTFE	Polytetrafluoroethylene coated on UP 316 SS[a]	Spray	0.5 ± 0.06	117.2 ± 0.4
Silicone	Silicone rubber ELASTOSIL® E 60 coated on Anodised Aluminium	Spray	0.13 ± 0.03	117.3 ± 0.5

a - Unpolished 316 stainless steel

b - Electropolished 316 stainless steel

Table 2. Contact angle of rapeseed and olive oil on different surfaces at 25°C

Surface	Oil	
	Rapeseed	Olive
UP 316 SS	17.7 ± 2.0	17.4 ± 0.3
ZrO_2 (UP 316 SS)	9.2 ± 0.3	8.5 ± 0.5
ZrO_2 (EP 316 SS)	15.5 ± 1.6	15.8 ± 0.4

Table 3. Cleaning ratings for different surfaces after frying turkey meat with oil at 200 °C

Surface Material	Use of oil for frying	Cleaning ratings (five repetitions)	t-value	Significance
UP 316 SS	Yes	3.4	2.59	P < 0.05
	No	2.4		
TiAlN (UP 316 SS)	Yes	4.0	5.18	P < 0.001
	No	2.0		
TiAlN (EP 316 SS)	Yes	2.0	*	*
	No	2.0		
ZrN (UP 316 SS)	Yes	2.2	0.52	ns
	No	2.0		
ZrN (EP 316 SS)	Yes	2.2	1.04	ns
	No	1.8		
ZrO_2 (UP 316 SS)	Yes	2.6	1.56	ns
	No	2.0		
ZrO_2 (EP 316 SS)	Yes	2.2	0.52	ns
	No	2.0		
QC (Al, Fe, Cr)	Yes	2.0	2.07	ns
	No	1.2		
PTFE	Yes	1.0	*	*
	No	1.0		
Silicone	Yes	1.0	0.52	ns
	No	1.2		

Average std.deviation on the ratings (five repetitions) - 0.61
*t-test cannot be carried out since the ratings are equal
ns - not significant

Technical University of Denmark ***Research and Innovation, PhD programme***

January 2010

Joint author statement

If a thesis contains articles made in collaboration with other researchers, a joint author statement about the PhD-student's part of the article shall be made by each of the co-authors, cf. article 12, section 4 of the Ministerial Order No. 18 February 2008 about the PhD degree

Title of the article:	Factors Affecting the Wettability of Different Surface Materials with Vegetable Oil at High Temperatures and its Relation to Cleanability		
Author(s):	Saranya Ashokkumar, Jens Adler-Nissen, Per Møller		
Journal:	Journal of Colloid and Interface Science		
PhD-student:	Saranya Ashokkumar	CPR-no.:	201185-3326
Signature of the PhD-student:		Date:	23 November 2010
Co-author:	Jens Adler-Nissen	Signature:	
Co-author:	Per Møller	Signature:	

Description of each author's contribution to the above-mentioned article:

Saranya Ashokkumar, as a first author, carried out the experimental work and have written the full manuscript. Jens Adler-Nissen and Per Møller as co-authors reviewed the full manuscript and gave comments and suggestions on the manuscript.

Fouling & Cleaning in Food Processing 2010

Proceedings of a conference held at
Jesus College, Cambridge, 22-24 March 2010

Edited by

D.I. Wilson and Y.M.J. Chew

Organised by

Department of Chemical Engineering and Biotechnology
University of Cambridge, UK

Centre for Formulation Engineering
University of Birmingham, UK

in collaboration with

IChemE Food & Drink Subject Group

Fouling, Cleaning and Disinfection in Food Processing 2010

Published by the Department of Chemical Engineering and Biotechnology, University of Cambridge, UK.

Printed by Print Out, High Street, Histon, Cambridgeshire

ISBN 978-0-09542483-2-1

Copies of this book may be obtained from

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CLEANABILITY EVALUATION OF DIFFERENT SURFACES BY FOULING FROM CONTACT FRYING OF FOODS

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ABSTRACT

The aim of this investigation was to evaluate the cleanability of different surfaces by fouling from contact frying of carrot, sweet potato and turkey meat (with and without the use of oil) at 200 and 240 □ C. The different surfaces investigated include 316 grade stainless steel (316 SS), polytetrafluoroethylene coated on 316 SS, silicone (silicone rubber Elastocil E60) coated on anodized aluminium, quasicrystalline coated on 316 SS and ceramics (zirconium oxide, zirconium nitride and titanium aluminum nitride) coated on unpolished and electropolished 316 SS. The cleanability of the various surfaces was rated by a standardized procedure developed by repeated experimental trials. The statistical calculation by ANOVA shows that there is a significant difference between the cleanability of different surfaces. The fouling from contact frying of different foods has found to have a strong influence on the cleaning properties of different surfaces and the use of oil has also found to have a remarkable influence on the easy-clean properties of the various surfaces. The results show that the cleanability of steel is enhanced by the different coatings. The topography of the surfaces was described by the profilometry and the electron microscope. The ceramics coated on electropolished 316 SS show enhanced cleanability when compared to ceramics coated on unpolished 316 SS due to the difference in their topography.

INTRODUCTION

In the modern food processing, foods are subjected to some form of thermal treatment before they are consumed. Cooking is a traditional way of thermally treating the foods. Frying is a unique process in cooking which gives the food a better taste and texture when compared to the boiled food. Frying process is often employed in the food industry to make ready-made products. During frying, food leave residues on the frying surfaces and hence fouling is a big problem in the food industries (Changani et al.,1997).

Stainless steel is a standard material used in the food industry. To overcome fouling problems, the stainless steel frying equipments are often coated with PTFE (polytetrafluoroethylene) due to its low surface energy, in order to make the surface non-stick to the food and for ease of cleaning of the surface after the frying process. In recent studies, different surfaces were analyzed in relation to reduced fouling. It was found by Gordon et al. (1968) that the PTFE - coated surface gave a higher recovery of milk deposits than on stainless steel pipes. However, PTFE - coated surface is always not the promising one in all the applications. Yoon and Lund (1994) analyzed different surface treatments of plate heat exchangers on milk fouling and found that there was no effect of surface materials on fouling and also concluded that there was no significant reduction of cleaning time on the PTFE - coated plate. Likewise, Kuisma et al. (2007) reported that the PTFE coating was not observed to be superior to uncoated and coated ceramic glazes in the cleaning of a soil mixture.

Studies were also carried out to evaluate the cleanability of open surfaces by developing biofilms on stainless steel surfaces (Wirtanen et al., 1995) and on floors and walls (Taylor and Holah, 1996). Boistier-Marquis et al. (2000) studied seven different floor samples fouled with six industrial soils and found that there was a significant difference in the cleanability of the different floor samples.

Several studies were carried out to evaluate the effect of surface treatment on cleaning of model food soils. Mauermann et al. (2009) used potato starch and whey protein solutions to assess the influence of surface modification on cleaning and showed that the starch deposits on Fluorinated Ethylene Propylene (FEP) modified surfaces were reduced by up to 76% and the protein deposits on nanocomposite modified surfaces (inorganic and hybrid coatings) were reduced by up to 34% in contrast to stainless steel. Saikhwan et al. (2006) studied the impact of different surface modifications of stainless steel on the removal of baked tomato paste using fluid dynamic gauging. Liu et al. (2006a) studied the effect of surface energy of different surfaces on the force required to remove tomato deposits. However, these studies did not reflect the effect of different surfaces on fouling from contact frying of foods at higher temperatures. The fouling resulting from contact frying of foods characterizes the actual fouling conditions prevailing in the food industry. It is necessary to evaluate the cleanability of different surfaces by fouling from frying of different foods since fouling from one food will be different from the other due to the difference in their composition. Hence our main aim was to compare the cleanability of different surfaces by fouling from contact frying of different kinds of foods which were carefully chosen according to their composition. The topography of the surfaces was described by the profilometry and the electron microscope. The effect of the topography of the different surface materials on their cleanability is also discussed in detail.

EXPERIMENTAL

Surfaces

All the frying discs were circular plates with a diameter of 90 mm and a thickness of 5 mm. In this study 10 different surfaces were investigated. The different surfaces investigated include 316 grade stainless steel (316 SS), PTFE, silicone, ceramics and quasicrystalline coatings. The ceramic coatings investigated include Zirconium Oxide (ZrO_2), Zirconium Nitride (ZrN) and Titanium Aluminium Nitride (TiAlN) coated on unpolished 316 grade stainless steel (UP 316 SS) and electropolished 316 grade stainless steel (EP 316 SS) substrates. The ceramic coatings, manufactured by Physical Vapor Deposition technique (PVD), were provided by Technological Institute, Aarhus, Denmark. PTFE coating, with its commercial name “Eterna”, spray coated on UP 316 SS substrate was supplied by Whitford Worldwide, Brescia, Italy. The silicone (silicone rubber ELASTOSIL® E 60) was spray coated on anodized Al-Mg 5754 aluminium substrate by Accoat A/S, Kvistgard, Denmark. The quasicrystalline coating with its commercial name “QC A5PM” was supplied by Saint-Gobain, France. The quasicrystallinic material was based on $Fe_xCr_yAl_z$.

Fouling

The frying discs were circular plates with a diameter of 90 mm and a thickness of 5 mm. The fouling is made on the frying discs, coated with different materials, by contact frying with three different foods such as turkey meat, carrot and sweet potato with and without the use of oil at 200 and 240 ° C. The foods were carefully chosen to represent the three main constituents of foods: proteins, carbohydrates and lipids. The composition of the different foods was taken from the Danish Food Composition Databank - www.foodcomp.dk.

- *(i)* *Turkey meat* was chosen to represent proteins. The composition of turkey meat was 75.5% water, 21.9% protein, 0% carbohydrates, 2.2% fat and 1% ash. The fresh meat was cut into approximately 1 – 1.5 cm thick flat pieces and frozen for an hour to cut the meat in proper shape. The meat was cut into round pieces which were about 4.0 cm in diameter and 1.5 cm in thickness.
- *(ii)* *Carrot* was chosen to represent simple sugars. The composition of carrot was 89.9 % water, 0.7 % protein, 8.8 % carbohydrates (5.9% sugar, 2.9% dietary fibre), 0.4 % fat and 0.7 % ash. The sweet potato was cut into rectangular pieces of about 5.0 x 2.0 cm with a thickness of about 0.1 cm.
- *(iii)* *Sweet Potato* was chosen to represent starch. The composition of sweet potato was 80.3% water, 1.3% protein, 17% carbohydrates (4.2% sugar, 10.1% starch, 2.7% dietary fibre) 0.3% fat and 1.1% ash. The sweet potato was cut into rectangular pieces of about 5.0 x 2.0 cm with a thickness of about 0.1 cm.
- *(iv)* *Rapeseed Oil* was chosen to represent lipids or fats. The composition of sweet potato was 0.0% water, 0.0% protein, 0.0% carbohydrates, 100% fat and 0% ash.

Contact frying is done with the frying table, a special construction made in our department workshop to perform the frying experiments. The temperature display in the frying table allows for monitoring the temperature at the centre of the frying table, as measured by the PT100 sensor. The fouling experiments were performed when the frying table is set at two different temperatures: 200 and 240 ° C. Once the frying table is stabilized after 30 minutes at the particular temperature, the frying surface is washed with water and dried. A good contact of the frying disc with the frying table is achieved by means of applying OKS Antiseize Copperpaste #240 (bought from Højstrup Industrilim) to the bottom of the frying disc using a paint brush. The frying disc is heated for 10 minutes and the surface temperature of the frying disc was noted by a contact thermometer. Then the food to be tested is placed on the frying disc and fried for 5 minutes on each side. If the experiment is to be done with oil, then the rapeseed oil is applied on both sides of the test item to be fried by a paint brush before frying. After the experiment the fouled frying disc is removed from the frying table and the cleanability of the frying disc is evaluated according to the cleaning procedure mentioned below.

Cleaning

An alkaline cleaning solution FOAM 235, commonly used in the food industry, was obtained from ITW Novadan ApS, Kolding, Denmark. FOAM 235 was a clear, colourless liquid containing 15-30% potassium hydroxide, <5% ethanol, <5% alkylpolyglycosid. The solution was diluted to 5% with water for all the cleaning experiments. The cleanability of the various surfaces was assessed by a standardized procedure and rated from a scale of 1 – 5 (Groll, 2002). The steps followed in the cleaning procedure were as follows: The fouled frying disc was (1) rinsed with water for 1 minute (2) soaked in the cleaning solution for 20 minutes and rinsed with water (3) scrubbed lightly using a yellow cleaning sponge and rinsed with water (4) scrubbed hardly using a yellow cleaning sponge and rinsed with water (5) scrubbed hardly using Scotch- Brite™ heavy duty scrub sponge and rinsed with water. A photograph of the frying disc was taken after each cleaning step. The surfaces were rated from 1 to 5 according to the following evaluation: 1 (if it is cleaned after one step) to 5 (if it is cleaned after step 5).

Roughness Profile

The two-dimensional roughness profile of the materials was measured using a Surftest SJ-201 Surface Roughness Tester (Mitutoyo, USA) according to Japanese Standards Association JIS B0601-1982. The 5 µm diamond stylus traverses on the test material at a speed of 0.25 mm/s. The downward force of the stylus was 4 mN and the measurement range was 350 µm. The cut-off length was 0.8 mm. Before each measurement, the instrument was calibrated using a reference work piece. Roughness (Ra), usually expressed in µm, explains the average height or depth of the peaks above and below the average centerline of a surface (Kuisma et al., 2007). The results were expressed as the mean of ten readings for each material.

Microscopy

The scanning electron microscope (FEGSEM 200F) was used to study the topography of the different surfaces. The photomicrographs were taken with a magnification of 10 µm using an accelerating voltage of 10 kV for all the examinations except for eterna and silicone coatings where 1 kV was employed to obtain photomicrographs with good resolution.

Statistical Analysis

The fouling and the subsequent cleaning experiments were repeated for 5 times. The influence of different surfaces, different foods, frying temperature and the use of oil for frying on the cleaning ratings were analyzed by ANOVA.

RESULTS

Easy-to-clean tests

The easy-to-clean ratings for all the surfaces are shown in Table 1. The statistical calculation by ANOVA shows that there is a significant difference between the cleanability of different surfaces ($p<0.01$). There is no significant difference between the repeated trials ($p>0.01$). The cleanability of stainless steel is enhanced by the different coatings. The difference in the composition of the ceramics has not produced a statistically significant difference on the easy-to-clean ratings ($p>0.05$). The cleanability of the ceramics coated on EP 316 SS shows a remarkable difference when compared to ceramics coated on UP 316 SS ($p< 0.05$).

The fouling from contact frying of different foods has found to have a strong influence on the easy-to-clean ratings of different surfaces ($p<0.01$). The temperature also has a significant effect on the easy-to-clean ratings ($p<0.01$). There is a clear statistical significance in the use of oil for contact frying of different foods on the cleanability of different surfaces ($p<0.05$).

Roughness and Microscopy

The value of roughness parameter, Ra, varied between 0.13 to 0.72 µm. The TiAlN coated on UP 316 SS has got the highest roughness value and silicone coating the lowest. The ceramics coated on EP 316 SS show a statistical difference in the roughness values when compared to ceramics coated on UP 316 SS ($p< 0.01$).

The photomicrographs of the different surfaces are shown in Figure 1. There is a distinct difference in the morphology of the electropolished stainless steel surface from the unpolished stainless steel surface. It is clear from the pictures that the topography of the ceramics coated on UP 316 SS is rougher than the same coated on EP 316 SS. The quasicrystalline, silicone and eterna coatings have a smooth morphology.

Table 1. Easy-to-clean ratings of the different surfaces by fouling from contact frying with (a) Turkey Meat (b) Carrot and (c) Sweet Potato at 200 and 240 □ C.

Substrate	Coating Material	Roughness Value Ra (µm)	Use of oil for frying	Easy- to-Clean ratings by fouling from contact frying with					
				Turkey Meat at		Carrot at		Sweet Potato at	
				200 □ C	240 □C	200 □ C	240 □ C	200 □ C	240 □ C
UP 316 SS	None	0.44	Yes	3.4	5.0	3.4	4.4	2.0	4.0
			No	2.4	3.0	2.6	4.2	1.2	2.0
UP 316 SS	TiAlN	0.72	Yes	4.0	4.2	3.4	4.8	2.0	2.4
			No	2.0	2.2	2.4	2.8	1.0	1.8
EP 316 SS	TiAlN	0.47	Yes	2.0	3.4	2.0	3.4	1.2	1.4
			No	2.0	1.8	1.6	2.4	1.0	1.4
UP 316 SS	ZrN	0.67	Yes	2.2	3.2	2.6	4.4	1.4	3.6
			No	2.0	2.8	2.2	3.4	1.4	1.2
EP 316 SS	ZrN	0.4	Yes	2.2	3.2	2.0	2.8	1.2	2.2
			No	1.8	2.2	2.0	2.0	1.0	1.2
UP 316 SS	ZrO_2	0.68	Yes	2.6	3.2	2.2	3.6	1.6	2.8
			No	2.0	2.4	2.0	3.8	1.4	1.4
EP 316 SS	ZrO_2	0.27	Yes	2.2	3.4	2.0	3.4	1.2	2.4
			No	2.0	2.0	1.8	2.6	1.0	1.0
UP 316 SS	QC A5PM	0.3	Yes	2.0	3.0	2.0	3.4	1.0	1.6
			No	1.2	1.4	1.6	2.0	1.0	1.2
Anodized Aluminum	Silicone	0.13	Yes	1.0	1.4	1.4	1.4	1.2	1.0
			No	1.2	1.6	2.0	3.0	1.4	1.0
UP 316 SS	Eterna	0.5	Yes	1.0	1.2	1.0	1.2	1.0	1.0
			No	1.0	1.0	1.2	1.6	1.0	1.0

4. DISCUSSION

Our study shows that the different surfaces have different extent of cleanability when fouled from contact frying of different foods at different temperatures. Our results show that the fouling from frying of different foods increases in the following order: sweet potato<carrot <turkey meat. In general, two types of adhesion mechanism can be proposed for the adhesion between the food and the frying surface: *chemical and mechanical adhesion*. Chemical adhesion is based on the chemical reactions, depending on composition of the food, taking place during thermal treatment of the food leading to the formation of chemical bonds between the frying surface and the food. Mechanical adhesion is based on the topography of the surface, like smooth or rough, depending on which the food can physically attach to the frying surface.

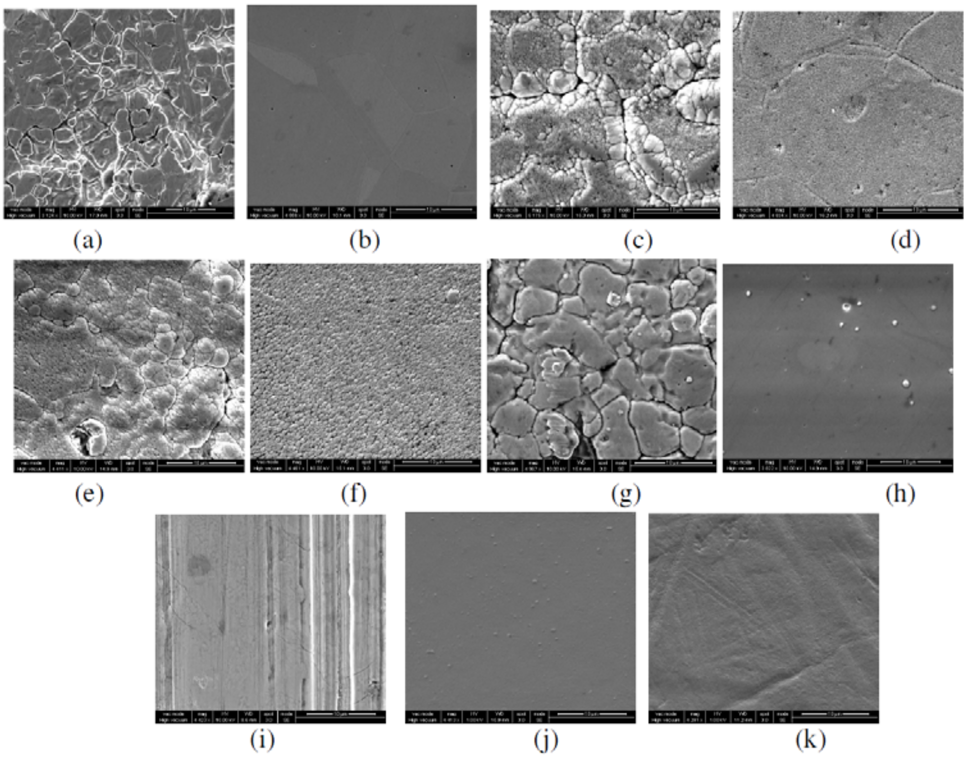

Figure 1. SEM photomicrographs of the different surfaces (a) UP 316 SS (b) EP 316 SS (c) TiAlN on UP 316 SS (d) TiAlN on EP 316 SS (e) ZrN on UP 316 SS (f) ZrN on EP 316 SS (g) ZrO_2 on UP 316 SS (h) ZrO_2 on EP 316 SS (i) QC A5PM on UP 316 SS (j) Silicone on anodized Aluminium (k) Eterna on UP 316 SS (All photomicrographs are taken with a magnification of 10 µm).

Sugar caramelization can be roughly divided into two stages, namely, decomposition and polymerization (Jiang et al., 2008; Richards & Shafizadeh 1978; Liu et al., 2006b). The first stage involves the breakdown of sugar to small molecules by dehydration, bond cleavage, retro-aldolization, etc. In the second stage radical polymerization, the predominating reaction in this stage, takes place forming more brown-coloured polymeric substances (Claude & Ubbink 2006). When sugar starts to caramelize the following compounds are formed in the subsequent reaction: caramelan, caramelen and caramelin (DeMan, 1999a). The splitting of glycoside bond is found to be the foremost reaction in the thermal degradation of sucrose which takes place at 185 °C and the thermal decomposition at 207 °C (Abd-Elrahman and Ahmed 2009). In the presence of proteins, carbonyl group present in sugar reacts with the free amine group in the proteins leading to maillard reaction. Increased temperatures have a marked effect on the Maillard reaction (Dutson & Orcutt 1984). It was suggested by several researchers that acrylamide in food results largely from the maillard reaction (Mottram et al., 2002; Stadler et al., 2002; Zyzak et al., 2003). Acrolein is found to be one of the precursors for acrylamide formation and acrolein gets oxidized to acrylic acid (Claeys et al., 2005).

During frying of carrot, fouling could be mainly from the caramelization of sugar or the products of Maillard reaction which usually looks brown in colour. Sweet potato contains less sugar and more starch when compared to the carrot. But the fouling from sweet potato is relatively less than the same from carrot. This could be due to the fact that the potato starch, being a polysaccharide, decomposes at a higher temperature of 306 □ C (Singh & Nath 2009) when compared to sucrose which decomposes at 207 □ C. It was discovered that the Maillard browning reaction may increase five to ten times for every 10 degree rise in the temperature if the foods contain fructose (DeMan, 1999b). In accordance with the Maillard reaction, the shorter the sugar chain, the more acrylamide was formed (Claeys at al., 2005). This reveals that more fouling from frying of carrot could be due to the reason that it contains larger amount of glucose and fructose, when compared to sweet potato, which leads to the formation of further Maillard browning reaction products.

Our results show that the fouling from frying of turkey meat was comparatively higher than the same from frying of carrot and the sweet potato. The cleanability of the surfaces also decreased when fouled with turkey meat. This is due to the high amount of protein content in turkey meat. Many studies revealed that fouling occurs due to the denaturation and aggregation of proteins (Bell and Sanders, 1944; Changani et al., 1997). It was also concluded from studies that the amount of fouling increases with the increase in protein concentration (Fryer et al.,1992). Studies showing the interaction between surface and protein deposit mentions that the initial protein fouling starts with adhesion at room temperature (Rosmaninho, et al., 2007). When they are heated, the protein starts to unfold and expose a free S-OH group in an activated state forming bond with the initially formed protein layer (Visser and Jeurnink, 1997). Studies indicate that interaction depends on the surface energy (Rosmaninho, et al., 2007). In our studies it shows that low energy surfaces are still fouled by protein content, but easy-to-clean when compared to the other high energy surfaces. This is due to the weak adhesion existing between the initial protein layer and the surface.

The use of oil for the frying process had a remarkable effect on the cleanability of the surfaces. When a oil is heated, several chemical reactions takes place. During heating, triglyceride molecule in a oil starts to decompose into fatty acids and glycerol. This glycerol and fatty acid can still decompose further during the heating. Glycerol forms acrolein during its decomposition which will further oxidize to form acrylic acid. A free radical is formed by the removal of hydrogen atom at the carbon atom next to the double bond. The subsequent propagation reaction results in the formation of a peroxide molecule by reaction with oxygen and finally the termination reaction yields non-active products, which is polymerized by cross linking between the fatty acid chains – principally the fat is cured. The formed acid directly attacks the surface. The free radicals formed during the frying process could also react directly with the active metal surface causing covalent bonds with the surface. Furthermore corrosion products formed by the acid attack on the surface can act as a catalyst for the polymerization of the unsaturated fatty acids. All these polymerization reactions caused by thermal effect plays a crucial role for the fouling process and the following cleanability of the surface.

Acrylic acid, as mentioned before and formed from these reactions will have an aggressive effect on the frying surface if the surface chemistry of the material is not inert. Hence, surface stability against chemical attack should be one of the prominent factors in selecting the frying surface. Ceramics, especially zirconium oxide (ZrO_2) is chosen since they have high bond energy between zirconium and oxygen. This is comparable to the bond energy of carbon and fluorine in PTFE.

The results show that the cleanability of the surfaces after fouling from frying of different foods decreases with increase in frying temperature. This is due to the fact that the rate of chemical reactions, that takes place during frying process, increases at higher frying temperatures.

The surface topography plays an important role on how the deposit layers will attach to the surface. Generally rougher surfaces with interlocking tendency are more prone for causing fouling of food. According to the Food Safety Regulations 1995, it was mentioned that the maximum roughness value for the hygienic surfaces should not be more than 0.8 µm. All the surfaces tested here have a roughness value less than 0.8 µm so according to hygienic perspective, all these surfaces are suitable for the food industry. Many studies indicated that there is no definite correlation between the roughness value and the cleanability (Yoon and Lund 1994; Plet 1992; Holah 1994). In our studies, even though a definite correlation could not be achieved, we found that the smooth surfaces gave a better cleanability than the rough surfaces. However, the roughness values will give only very little information about the true topography of a surface and the presence of porosities or scratches (Hilbert et al., 2003). Hence it is always not easy to correlate the cleaning efficiency only with the roughness measurements. Hence techniques like SEM will help to characterize the true topographic profile and defects of the surfaces (Hilbert et al., 2003).

The electron microscopy pictures clearly indicate that the topography of the surfaces affects the cleanability of the surfaces. The silicone, eterna and QC PM5 coating have a smooth morphology which gives better cleanability than the other surfaces. The photomicrograph of the UP 316 SS shows that there is lot of defects or grooves in the surface caused of the grain boundaries, when compared to the smooth EP 316 SS. Hence the ceramics coated on EP 316 SS have a smoother morphology when compared to the same coated on UP 316 SS. This is due to the fact that the ceramic coating cannot completely fill the voids on the UP 316 SS, but this is eliminated when the stainless steel substrate is electropolished before the application of the coating. Our finding shows that the cleanability of the ceramic surfaces coated on EP 316 SS gave a better performance than the same coated on UP 316 SS. When there are defects or grooves in the surface, a food can physically attach (inter lock) to the defects and hence making the cleaning process difficult – furthermore by reusing the surface, fouling left back can act as bonding sites for additional fouling.

5. CONCLUSION

Our finding shows that there is a difference in the cleanability of different surfaces by fouling from contact frying of different foods at different temperatures. The frying temperature and the use of oil for the frying process have found to have a strong influence on the cleanability of the different surfaces. The surfaces with low roughness value gave a better cleanability than the surfaces with high roughness value. The electron microscopy picture reveals that the surfaces with a smooth morphology and surfaces which are free of defects are found to have better cleaning properties. The roughness parameters alone cannot characterize a surface that can be suitable for a frying process. The surface to be used for a frying process should be subjected to field tests and can be selected after careful consideration in all terms. The surface to be used for a frying process should be chemically inert as well as mechanically compatible to reduce the cleaning efforts in food process plants.

ACKNOWLEDGEMENTS

We would like to acknowledge the financial support from the Ministry of Science and Technology, Denmark. The authors thank the suppliers of different surface coatings.

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Technical University of Denmark **Research and Innovation, PhD programme**

January 2010

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If a thesis contains articles made in collaboration with other researchers, a joint author statement about the PhD-student's part of the article shall be made by each of the co-authors, cf. article 12, section 4 of the Ministerial Order No. 18 February 2008 about the PhD degree

Title of the article:	Cleanability evaluation of different surfaces by fouling from contact frying of foods		
Author(s):	Saranya Ashokkumar, Birgitte R.Thomsen, Jens Hinke, Per Møller, Jens Adler-Nissen		
Journal:	Proceedings of Fouling and Cleaning in Food Processing 2010		
PhD-student:	Saranya Ashokkumar	CPR-no.:	201185-3326
Signature of the PhD-student:		Date:	19 November 2010
Co-author:	Birgitte R.Thomsen	Signature:	
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Description of each author's contribution to the above-mentioned article:

Saranya Ashokkumar, as a first author, carried out the experimental data analysis and have written the full manuscript. The experimental work has been carried out by Birgitte R.Thomsen (second author). Jens Hinke, Per Møller and Jens Adler-Nissen as co-authors reviewed the full manuscript and gave comments and suggestions on the manuscript.

Modelling of Coupled Heat and Mass Transfer during a Contact Baking Process

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Abstract- A mathematical model of coupled heat and mass transfer of a contact baking process is developed. In the current model formulation, a local evaporation of water is described with a reaction-diffusion approach, where a simultaneous diffusion and evaporation of water takes place. The resulting coupled model equations (unsteady state heat transfer, liquid water and water vapour) were solved using the Finite Element Method (*COMSOL Multi-physics® version 3.5*). During the baking process, local temperatures and overall moisture loss were measured continuously. The model – predicting temperature, liquid water content in the product and water in the vapour phase– was calibrated and partially validated using data obtained during baking of a representative food model (a pancake batter) under controlled conditions on a specially designed experimental rig. The unknown parameters in the model equations were estimated using the standard least squares method by comparing the measured with the predicted temperature profile. Good agreement was achieved between model predictions and the experimental values.

***Key words**: Contact baking process, Evaporation, Finite Element Method, Heat and mass transfer, Modelling*

1. Introduction

Contact baking is a widely applied process used in for example baking of crisp bread, tortillas, pizzas, chapatti, pancakes, pita breads etc. Being a traditional process, optimization and process control to obtain the desired final product quality is still largely based on experience and good craftsmanship rather than on predictive, engineering calculations. A transition from this traditional empirical approach towards methods that rely on calculations based on predictive models requires a deeper mechanistic understanding of the contact baking process and a knowledge of the physics involved, particularly heat and mass transfer. During the baking process heat and mass transfer occur simultaneously and induce many complex physical-chemical processes such as evaporation of water, crust formation, browning reactions, denaturation of proteins, and gelatinization of starch, (Lee et al., 1996; Mondal and Datta, 2008; Sablani et al., 1998; Therdthai and Zhou, 2003). In the literature, there are only a few publications on the modelling of contact baking (Gupta, 2001) and the related contact frying process (Pan et al., 2000; Pan and Singh, 2002; Wichchukit et al., 2001), as compared to baking in a convection oven. In this paper, we have chosen a mechanistic model as the framework to represent available knowledge on heat and mass transfer in the contact baking process.

A mechanistic mathematical model of heat and mass transfer should take into account the main phenomena explaining the physical behavior of the product during the contact baking process. In the present work, we will therefore develop a model for one-sided contact baking, where we have chosen a thick pancake as a representative food model. One-sided contact baking is a very common type of contact baking. In one-sided contact baking, heat is transferred to the product – placed on a specially designed heating rig for the experiments reported in this manuscript – by conduction from a hot surface. During the contact baking process, multi-phase water transport (liquid water and water vapour) and phase change (evaporation) occur; these processes are coupled and interact with each other during the baking process. The objective of this work is to present a detailed mechanistic mathematical model of the coupled heat and water transport during the contact baking process, and to validate that model with experiments.

Nomenclature

c_{pp}, and c_{pAl},	Specific heat capacity (J/(kg·K) of product (batter), and aluminum, respectively
D_l and D_v	Liquid and vapour diffusion coefficient (m^2/s), respectively
E_a	Activation energy (kJ/mol)
h_{bot}	Overall heat transfer coefficients at bottom boundary (baking disc-frying rig interface)
H_{evp}	Latent heat of evaporation (J/kg)
h_{top}	Heat transfer coefficients at top surface at air-product interface (W/(m^2·K))
k_{evp}	Evaporation rate constant at the evaporation temperature (1/s)

k_l *and* k_v	Liquid and vapour mass transfer coefficient (m/s), respectively
k_p, k_{Al}, *and* k_{air}	Thermal conductivity (W/(m·K)) of product, aluminum, and air, respectively
M_w	The molecular weight of water (kg/mol)
R_{evp}	Rate of evaporation (kg/(kg·s))
R_g	The gas constant (J/K·mol)
T	Temperature (K)
t	Time (s)
T_{air}	Surrounding air temperature (K)
T_{evp}	Evaporation temperature (K)
T_{set}	Heating rig temperature set point (K)
X_l *and* X_v	Liquid and vapour water content (kg of water/kg dry solid), respectively
y_i	The mass fraction of each component (water, protein, carbohydrate and fat) (kg/ kg of sample)
z	The position in the z direction
ρ_p, ρ_s, ρ_{Al} *and* ρ_{air}	Density (kg/m^3) of product (bulk), solid, aluminum, and air, respectively
ε	Porosity, dimensionless
Subscripts	
air	Air
Al	Aluminum
l and v	Liquid and vapour, respectively
p	Product (pancake batter)
exp	Experimental
SD	Standard deviation

2. Model of Mass and Heat Transfer

2.1 Descriptions of the process and model formulations

Contact baking is a thermal process, where the product is heated at high temperature (140°C to 300°C) by contact with a hot surface. In the present work, the product (pancake batter) is heated on a horizontal heating rig, where heat is transferred by conduction through several layers of materials. These layers of materials include: (1) the heating rig (see 3.2), (2) thermal conducting paste, and (3) bottom surface of the baking disc, which is made of aluminum (Al), as shown in Fig.1a. For the remaining part of this paper, the term 'heating rig' will be used when referring to the rig and the thermal conducting paste together (1 and 2, in Fig. 1a). The heat transfer causes a rapid raise of the temperature within the pancake batter, which induces water migration by diffusion and evaporation. Heat and mass transfer interact via evaporation (Huang et al., 2007). The most important phenomena influencing key process variables (temperature, concentration of liquid water and concentration of water vapour) within the pancake batter are described in Fig. 1b.

The following assumptions were made when developing the model: a) heat is transferred within the pancake batter by conduction in the beginning (later, evaporation and partial condensation also contribute to heat transfer, see item c and e); this is reasonable, because the pancake batter is rather viscous and its thickness is relatively low (no natural convection); b) heat is lost from the product to the surrounding air via convection: rough calculations indicate that the radiation can be neglected because the surface temperature of the product is below 100 °C, (the measured temperature at position A, 6.4 mm from the bottom, only 1.6 mm from the top surface is well below 100 °C); c) the liquid water is transferred by diffusion within the pancake batter and simultaneously local evaporation takes place; d) liquid water and water vapour transport through the product are considered separately as multi-phase transport; e) the water vapour is generated within the pancake batter, then it migrates to the top surface (water-air interface, at $z = z_5$, Fig. 1a) and subsequently diffuses to the external environment (air); f) a transient one dimensional model (only heat and mass transfer in the z direction) is considered. This assumption is valid, because the diameter (2R = 90 mm) of the pancake batter is very large compared to the height (z_5 = 8 mm), and the effect of heat flux from the sides (in x and y directions) is small compared to the effect of heat flux from the bottom.

2.2 Governing model equations

2.2.1 Heat transfer

Heat transfer within the pancake is treated as a problem of transient heat conduction with phase change that includes evaporation of water. Using the conservation of energy, the governing equation for the heat conduction with phase changes within the pancake batter (domain 5 in Fig. 1a) is given by Eq. (1). A similar formulation was also used by Huang et al. (2007) to model the bread baking process.

$$\rho_p c_{p,p} \frac{\partial T}{\partial t} = \frac{\partial}{\partial z}\left(k_p \frac{\partial T}{\partial z}\right) - \rho_s R_{evp} H_{evp} \tag{1}$$

where T is the temperature (K), t is time (s), k_p is the thermal conductivity of the product (W/(m·K)), $c_{p,\mathrm{p}}$ is the specific heat capacity of the product (J/(kg·K)), ρ_p and ρ_s are the density of the product and of the dry solid (kg/m^3), respectively, H_{evp} is the latent heat of evaporation (J/kg), and R_{evp} is the rate of evaporation (kg of water/(kg of solid·s)), (see section 2.3.1). The above formulation, Eq. (1), incorporates the local evaporation of water (the second term on the right-hand side), and it represents the heat dissipated by evaporating the water.

Heat transfer through the bottom surface of the baking disc (domain 3 in the Fig. 1a) is given by:

$$\rho_{Al} c_{p,Al} \frac{\partial T}{\partial t} = k_{Al} \frac{\partial^2 T}{\partial^2 z} \tag{2}$$

where ρ_{Al}, $c_{p,Al}$ and k_{Al} are the density, specific heat capacity, and thermal conductivity of the Al, respectively.

The following boundary conditions apply for heat transfer:

The heat flux from the heating rig to the baking disc (at z = -z$_3$):

$$-k_{Al} \left.\frac{\partial T}{\partial z}\right|_{z=-z_3} = h_{bot}\left(T_{set} - T\right) \tag{3}$$

At the bottom of the pancake batter surface (z = 0, pancake batter-baking disc interface), the net heat flux at the interface is equal to the heat of evaporation at the interface:

$$q_3\big|_{z=0} - q_5\big|_{z=0} = q_{evp}\big|_{z=0} \tag{4}$$

At the top surface of the pancake batter ($z = z_5$, pancake-air interface), heat is exchanged with the surrounding air by convective heat transfer:

$$-k_p \frac{\partial T}{\partial z}\bigg|_{z=z_5} = h_{top}\left(T - T_{air}\right) \tag{5}$$

where T_{air} and T_{set} are the surrounding air temperature (K) and the frying rig's temperature set point, respectively, h_{top} is the heat transfer coefficient at the top surface, i.e. at the air-product interface (W/(m^2·K)), and h_{bot} is the contact heat transfer coefficient at the bottom boundary (at the heating rig-baking disc interface), q_3, q_5 and q_{evp} are the heat flux at z = 0, from domain 3, to domain 5 and through evaporation at the interface, respectively.

2.2.2 Mass transfer

Liquid water transport: The governing liquid water transport within the product (domain 5, in Fig. 1a) is given by Eq. (6) (Huang et al., 2007):

$$\frac{\partial X_l}{\partial t} = D_l \frac{\partial^2 X_l}{\partial^2 z} - R_{evp} \tag{6}$$

Water vapour transport: The governing equation for water vapour transport within the dough is given by Eq. (7), (Huang et al., 2007):

$$\frac{\partial X_v}{\partial t} = D_v \frac{\partial^2 X_v}{\partial^2 z} + R_{evp} \tag{7}$$

where X_l, and X_v are liquid and vapour water content on a dry basis (kg of water/kg of solid), respectively; D_l and D_v, are the liquid and vapour diffusion coefficient (m^2/s), respectively; and t is time (s). The sign of the source term, R_{evp}, is negative in Eq. (6) and is positive in Eq. (7), i.e liquid water disappears, while water vapour is generated during the baking process. When, R_{evp} is zero there is no local evaporation.

In the domain 3, there is no mass transfer.

The following boundary conditions apply for mass transfer:

At the bottom surface of the pancake batter (z = 0), the rate of liquid water removal from the pancake batter, the rate of water vapour generation and the rate of evaporation are equal, Eq. (8).

$$-D_l \left.\frac{\partial X_l}{\partial z}\right|_{z=0} = D_v \left.\frac{\partial X_v}{\partial z}\right|_{z=0} = -\left.\frac{q_{evp}}{H_{evp}\boldsymbol{\rho}_s}\right|_{z=0} \tag{8}$$

At the top surface ($z = z_5$): the boundary conditions for liquid water and vapour are given by Eq. (9) and (10), respectively

$$-D_l \left.\frac{\partial X_l}{\partial z}\right|_{z=z5} = k_l\left(X_l - X_{l,air}\right) \tag{9}$$

$$-D_v \left.\frac{\partial X_v}{\partial z}\right|_{z=z5} = k_v\left(X_v - X_{v,air}\right) \tag{10}$$

where k_l and k_v are the liquid and vapour mass transfer coefficient (m/s), respectively.

2.3 Constitutive equations

2.3.1 Evaporation rate

A phase change from liquid water to water vapour is considered as a heterogeneous reaction with first order kinetics (Peters et al., 2002), where the evaporation rate is based on the Arrhenius equation. The basic Arrhenius equation for the rate of evaporation incorporates varying water content and temperature dependence. However, the limitation to the basic Arrhenius type equation when used for the evaporation rate is that it induces evaporation of water at low temperature in the model (temperature far below the evaporation temperature), which is not the case in practice. Here a modified rate equation has been adopted by considering the fact that the evaporation takes place around the evaporation temperature. The modified rate equation which mathematically takes the same form as the Clausius–Clapeyron equation, for the evaporation rate near the evaporation temperature, T_{evp}, is given by:

$$R_{evp} = k_{evp} X_l \underbrace{\exp\left(-\frac{E_a}{R_g}\left(\frac{1}{T} - \frac{1}{T_{evp}}\right)\right)}_{f phase} \qquad (11)$$

where k_{evp} is the evaporation rate constant at the evaporation temperature (1/s), R_g is the gas constant (J/(K·mol)), E_a is the activation energy (J/mol). Evaporation of water utilizes evaporation enthalpy, and then $E_a = H_{evp} M_w$ and M_w is the molecular weight of the water (kg/mol), T_{evp} is the evaporation temperature (K) (reference temperature), and f_{phase} is a function that describes the phase change coefficient.

Equation (11) can describe the evaporation rate, because 1) at lower temperatures (far below T_{evp}), the value of f_{phase} is close to 0, and thus the rate of evaporation is close to zero. On the contrary, when T is close to T_{evp}, the value of f_{phase} is close to 1, and the rate is close to the rate at T_{evp}, 2) when equation (11) is combined with the above governing model equations (1), (7), and (8), the resulting set of equations describes the heat and mass transfer during the contact baking process for the entire heating period (heating and evaporation phase), without any discontinuity. Thus it eliminates numerical problems as well. In this study, the value of the parameter k_{evp} (rate constant of evaporation) is estimated together with the other unknown parameters by comparing the numerical results of the current model with measured experimental data as described in section 3.4.

2.3.2. Thermo-physical properties

Thermo-physical properties are given in Table 1 (appendix A).

3 Materials and methods

3.1 Sample preparations

Pancake batter was prepared by mixing 50 g egg white, 30 g egg yolk, 150 g of milk, 125 g of wheat flour and 20 g of sugar. For every baking experiment, 50 g of pancake batter was used to make a pancake with an approximate thickness of 8 mm.

The initial composition of the pancake was estimated from the composition of the ingredients, and was found to be 56.1% water, 6.9 % protein, 33.8 % carbohydrate and 3.2 % fat (% w/w, mass basis). For cross-validation, a dry matter analysis was made to determine the initial water content in the pancake batter. The water content (%w/w) of the pancake batter was measured by drying for 24 h at 105 ^{o}C (Nielsen 1994) and found to be (55.6 ±0.2) %, (mean ± SD). The small difference (0.5%) between the calculated and the measured water content may be due to a slight evaporation loss during the mixing of the ingredients.

3.2 Baking and experimental setup

***Heating rig*:** The heating rig was constructed with a 300 x 300 x 25 mm aluminium slab cast of the alloy AA-6082 (AlMgSi1). The aluminium slab was placed on a thermostated hot-plate of 300 x 300 mm (KR433-U12, Svend Nielsen A/S, DK) which has a maximum capacity of 3 KW. A PT100, class B temperature sensing resistor in a flexible stainless steel sheath (IEC60751, Labfacility, UK) is inserted into a hole which is drilled into the centre of the aluminium slab. The sides and bottom of the heating rig are insulated with Fiberfrax Duraboard MD, 50mm (Unifrax, UK). The heating rig temperature set point was controlled within +/- 1^{o}C with a proportional–integral–derivative controller (PID controller) for temperature set points in the range of 100 ^{o}C to 300 ^{o}C. The entire heating rig is placed on a balance (Signum 1, Sartorius, VWR, DK). The balance has a maximum capacity of 35 kg and an accuracy of 0.1 g. The balance is connected to a computer to allow continuous monitoring of the mass. The mass data is recorded every second by the program Sartoconnect (version 3.5).

***Baking disk and position of sensors*:** A circular baking disc with a diameter of 90 mm and a thickness of 5 mm (z_3) was used for the pancake baking experiments. The experimental set up is shown in section 2.1 (Fig. 1). The baking disc is made of 5754-aluminum (domain 3, Fig 1a). A removable stainless steel ring (domain 4, Fig. 1a) was made to fit to the aluminum disc during baking experiments. The higher thermal expansion of aluminum as compared to stainless steel results in expansion of the aluminum plate during heating such that it fits tightly to the stainless steel ring when the plate is heated.

To fix the temperature sensors at a given position within the pancake batter, a temperature sensor holder (E) was constructed at the center of the baking disc, as shown in Fig. 2. Four holes were made through the sensor-holder (E), which is made of Teflon. In each hole, temperature sensors

(T-type thermocouples) were placed at four different positions (A = 6.4 mm, B = 4.8 mm, C = 3.2 mm and D = 1.6 mm, measured as the distance from the bottom surface), as illustrated in Fig. 2. The weight of the baking disc within the above setup (baking disc and temperature sensor holder and four sensors) was measured separately. Then, approximately 50 g of pancake batter was taken from the pre-prepared pancake batter (see section 3.1) and gently added into the baking disc. The initial weight was then recorded. The pancake batter sample with sensors and baking disc were finally placed on the heating rig and the pancake batter sample was baked for 20 minutes. This procedure was repeated for all the samples, each time performing all the measurements (weight loss and temperature measurements).

3.3 Data collection/measurement

All the temperature sensors (T-type thermocouples) were connected to the computer with data logger (Tc-08 Pico Technology, Cambridgeshire, UK) where the temperature is recorded every second. At the same time, mass loss due to evaporation was monitored continuously by recording the weight every second, using the set up described in section 3.2.

3.4 Effect of heating rig temperature

The temperature and mass measurements were performed at three different temperature set points (160, 200 and 240 ºC) (see section 3.2). The measurements were repeated four times for each temperature set point. Average temperature and water content profiles – where the latter was obtained from mass loss data – were computed for each temperature set point.

3.5 Model solution, calibration and validation

The model equations were solved in COMSOL using the *Finite Element Method*. The set up in COMSOL consists of two domains: the product (domain 5, in Fig. 1) and the baking disc (domain 3, in Fig. 1). The governing equations of heat and mass transfer with their constitutive equations and initial values were set for each domain. The initial values were obtained from the measurements; the values of the input parameters used in the model are given in appendix B. The model was calibrated and validated using the available experimental data (measured temperature, see section 3.3a) obtained during the baking of the model food. The temperature measured at position A was used for parameter estimation while the remaining temperature measurements were used for model validation. The unknown parameters in the model were estimated using the least squares method by comparing the simulated and experimental temperature profiles. The resulting solution of the parameter estimation problem is a set of model parameters which minimizes the value of the objective function. The objective function is the sum of the squared differences between the simulated temperature (T_A) and the measured temperature profile ($T_{A,exp}$). The measured and simulated temperature values were taken at 10 seconds sampling intervals. For the minimization of the objective function, the Trust-Region Methods numerical algorithm (within the Matlab® environment), suited for nonlinear estimation problems, was used. The model solution, calibration and validation were implemented in the *COMSOL-Matlab®* ***version 3.5*** interface environment.

4. Results and discussion

4.1 Experimental temperature profile

The measured temperature profiles at different positions within the pancake batter (positions A, B, C and D, respectively) for the three temperature set points are plotted in Fig. 3. Generally, two major distinct periods can be distinguished in the temperature profiles: the heating period (sensible heat dominant zone) and the evaporation period (latent heat dominant zone).

In the heating period (preheating), most of the supplied heat energy (from the heating rig) is used to rise the temperature of the product (pancake batter). The heating period is short compared to the evaporation period, particularly for the position in the product that is closest to the bottom surface (e.g. at position D, about 200 s, Fig. 3 top-left).

During the evaporation period, where the temperature curves only rise slowly, nearly all of the supplied heat to the product is used for evaporating the water. In the evaporation period, with a temperature set point of 160 ^{o}C, the temperature at position C is more or less stable around the boiling point of water (attains $T = 100\ ^{o}C$ *at* $t = 600\ s$), while towards the end of the baking process, there is a slight temperature rise ($t = 1200\ s$, $T = 103\ ^{o}C$). For the same temperature set point of 160 ^{o}C, however, the temperatures at the positions A and B remain below 100 ^{o}C for the entire period of baking. Also, they remain almost constant (*approximately at* $T_A = 89\ ^{o}C$ *and* $T_B = 95\ ^{o}C$, *respectively*) for most of the heating time. The length of the period in which this constant temperature level is observed, is getting shorter as temperature sensor position moves from the top to the bottom surface.

At position D, in the evaporation period, an early rise of the temperature above 100 ^{o}C was observed. The early rise in temperature above the boiling point of water is explained by the drying-out effect at the bottom surface due to vigorous evaporation. This means that, as the liquid water content diminishes near the bottom surface: (1) an insulating layer is formed at the bottom surface, which reduces the thermal conductivity, and in turn the thermal diffusivity; and (2) less and less energy is consumed by evaporation at the bottom surface layer, compared to earlier times where the concentration of water was higher. This effect is more pronounced with higher temperature set points, especially at position D (Fig. 3).

4.2 Effect of temperature set point

In the heating period, the temperature profiles with the three temperature set points follow each other and there is only a slight difference in temperature profile between each temperature set point (Fig. 3). However, in the evaporation period, the three temperature set points have resulted in different product temperature profiles. This is particularly the case at position D (Fig. 4, top-left). The increase of the temperature set point leads to a higher evaporation rate, and as a consequence a faster drying out, which in turn induces a temperature rise. Towards the end of the baking process (t = *1200 s*), the product temperature at position D attains a temperature of 112 ^{o}C , 127 ^{o}C and 148 ^{o}C, with temperature set points of 160 ^{o}C, 200 ^{o}C and 240 ^{o}C, respectively. The temperature profile of the product closer to the bottom surface is very sensitive to the temperature set point, while this sensitivity decreases as the position of the temperature sensor is further away from the bottom surface (Fig. 3, compare at four positions, D to A). The effect of the temperature set point on the product temperature profile at position A is quite small compared to the effects observed at position D. Besides, the spatial variation of temperature (temperature gradient) in the pancake batter is relatively smaller with lower temperature set point compared to higher temperature set points. This implies that the quality of the end product related to temperature, is more uniform when baked at a lower temperature set point compared to a higher temperature set point.

Fig. 4 shows the corresponding average water content of the product when baked at the three temperature set points (160 ^{o}C, 200 ^{o}C, and 240 ^{o}C). The average water content of the product decreases as a function of time. In the early stages of the experiment ($t < 200$ s), the rate of decrease is relatively low, and visually there is no difference between the three average water content profiles. The turning point for the rate of decrease is around $t = 200$ s, when the bottom region of the product has reached the evaporation temperature (Fig. 3, at position D). After that time, $t = 200\ s$, the average water content of the product decreases rapidly, and the rate is different for the three temperature set points (Fig. 4). The rate of evaporation, and thus the rate of weight loss, increases with increasing temperature set point. The latter is convincingly illustrated by the average slopes of the water content profiles: $(-1.4,\ -2.3 \text{ and } -3.8) \cdot 10^{-4}$ kg/kg/s, for a temperature set point of 160 °C, 200 °C, and 240 °C, respectively.

4.3 Model calibration and validation

Model calibration: The model equations of heat and mass transfer developed in section 2 were solved and the unknown parameters of the model were estimated. The parameters (k_{evp} and h_{bot}) were estimated by fitting the simulated temperature profile to the data available for position A ($T_{set} = 160$ °C). The estimation results, presented as nominal value ± confidence interval of the parameter, are: $k_{evp} = (11.4 \pm 0.2) \cdot 10^{-5}$ and $h_{bot} = 360.7 \pm 12.8$. The model fit is shown in Fig. 5.

Model Validation: The model was validated by comparing the simulated and measured temperature profiles at the three other positions (B, C, and D), using the parameters estimated on the basis of the data collected at position A. Results of that validation are presented in Fig. 6 ($T_{set} = 160$ °C), and show a good agreement between simulated and measured temperature profiles at positions B and C. At position D, the simulated and measured temperature profile show a good agreement for the heating period, but there is a clear deviation between the simulated and measured temperature profile in the evaporation period (Fig. 6, at position D). This deviation is assumed to be due to: (1) the burning and crust formation at the bottom surface, which is not well-described in the model; (2) uncertainty on the sensor position: the sensor at position D is less stable compared to the temperature sensors at other positions. Indeed, around $t = 200$ s the sensor position (D) might move slightly upward as a result of vigorous water vapour generation which can create upward pressure.

Moreover, the model was validated by comparing the simulated and measured temperature profile at other temperature set points (200 ^{0}C and 240 ^{0}C) at position A (Fig. 7) and B (Fig. 8). The simulated results in Fig. 7 and Fig. 8 were obtained on the basis of the model for the three temperature set points with all the same settings (as above, obtained in the model calibration, T_{set} = 160 °C), except that the thermal conductivity for the set points 200 °C and 240 °C is reduced by 10% compared to the value at the set point of 160 °C. The reduced value of the thermal conductivity for higher temperature set points is motivated by the increased insulation effect at the bottom surface. This insulation effect, due to drying out and crust formation, is compensated in the model by reducing the thermal conductivity value. The higher temperature set point creates a thicker insulating layer at the bottom surface of the product, which means higher resistance, or lower thermal conductivity in the case of higher temperature set point.

5. Conclusion and perspectives

In this work, a mathematical model of coupled heat and mass transfer of a contact baking process was developed, taking into account multiphase water transport and local evaporation. The developed model gives a good understanding of the contact baking process, by predicting the temperature and water content profile within the product. A good agreement between the measured and the predicted temperature profile was obtained at positions A, B, and C, which allows us to conclude that the developed model of heat and mass transfer is suitable for describing the contact baking process. Moreover, the experiments also showed that the temperature set point has a significant effect on the product, and more specifically on the obtained temperature profiles and the mass loss.

The developed model of heat and mass transfer is a useful tool in developing an improved process, where it can be used in the optimization of the contact baking process by performing 'in silico' experiments, for example to study the effect of different process parameters on the baking process. Moreover, the developed process model can in principle be integrated with other quality attribute models as well, in order to perform further optimization of the contact baking process. For example, browning reactions take place in the product during baking, where temperature and water content are two important factors responsible for the change of color (Zanoni, et al., 1995; Purlis, 2010) due to such browning reactions. To study such phenomena the kinetics of the browning reactions could be integrated with the heat and mass transfer model presented here.

Acknowledgement

Aberham Hailu Feyissa would like to thank DTU for a Ph.D. grant under the aegis of Food-DTU.

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Appendix

A. *Thermo-physical properties* (Rao et al., 2005)

Table 1 Thermo-physical properties

***Density* :** $\rho = \dfrac{1-\varepsilon}{\sum_i \dfrac{y_i}{\rho_i}}$ (A.1) y_i is the mass fraction of each component (water, protein, carbohydrate and fat), kg /kg of sample and ε is the porosity of the product
***Specific heat capacity of product*:** $c_p = \sum c_{p_i} y_i$ (A.2) $c_{p_i} = c_o + c_1 T - c_2 T^2$ Where c_0, c_1 and c_2 are coefficients for the heat capacity of the components
Thermal conductivity (function of moisture content): $k_p = k y_w + \varepsilon k_{air}$ (A.3) Conversion between the X(kg of water/kg solid) and y_w (kg of water/kg of sample): $y_w = X / (1+X)$ (A.4)

B. *Input parameter values*

Table 2 Input parameter values

parameter	value	parameter	value	parameter	value
$y_{p,o}{}^{b}$	0.07 kg/kg	$\rho_f{}^{d}$	920 kg/m^3	$D_v{}^{e}$	$8\cdot10^{-7}$ m^2/s
$y_{c,o}{}^{b}$	0.33 kg/kg	$\rho_p{}^{d}$	1320 kg/m^3	$D_l{}^{g}$	$1\cdot10^{-9}$ m^2/s
$y_{f,o}{}^{b}$	0.03 kg/kg	$\rho_c{}^{d}$	1600 kg/m^3	k^{d}	0.65 W/(m·K)
$X_{lo}{}^{a}$	1.25 kg/kg	$\rho_w{}^{d}$	1000 kg/m^3	$X_{l,air}{}^{c}$	0 kg/kg
$T_o{}^{a}$	293.15 K	$\rho_s{}^{b}$	1467 kg/m^3	$k_{air}{}^{d}$	0.023 W /(m·K)
$z_5{}^{a}$	0.008 m	$\rho_{Al}{}^{f}$	2660 kg/m^3	$k_l{}^{e}$	$2.3\cdot10^{-11}$ m/s
$z_3{}^{a}$	0.005 m	$c_{pAl}{}^{f}$	960 J/(kg·K)	$T_{set}{}^{c}$	433.15 K (160 °C)
R_g	8.314 J/(K·mol)	$k_{Al}{}^{f}$	150 W/(m·K)	$T_{air}{}^{a}$	308.15 K (35 °C)
M_w	0.018 kg/mole	$X_{v,air}$	0.0062 kg/kg	$T_{evp}{}^{c}$	373.15 K
H_{evp}	$2.3\cdot10^{-6}$ J/kg	$k_v{}^{e}$	$9.6\cdot10^{-5}$ m/s	$h_{top}{}^{b}$	8 W/(m^2·s)

Superscripts:

a: measured *b: calculated or estimated*

c: set (assumed) *d:* (Rao et al., 2005)

e: Obtained from (Thorvaldsson and Janestad, 1999) *f: Obtained from* (Martienssen and Warlimont, 2005)

g: (Toledo,1991)

Subscripts:

p: protein *c: carbohydrate* *f: fat* *w: water*

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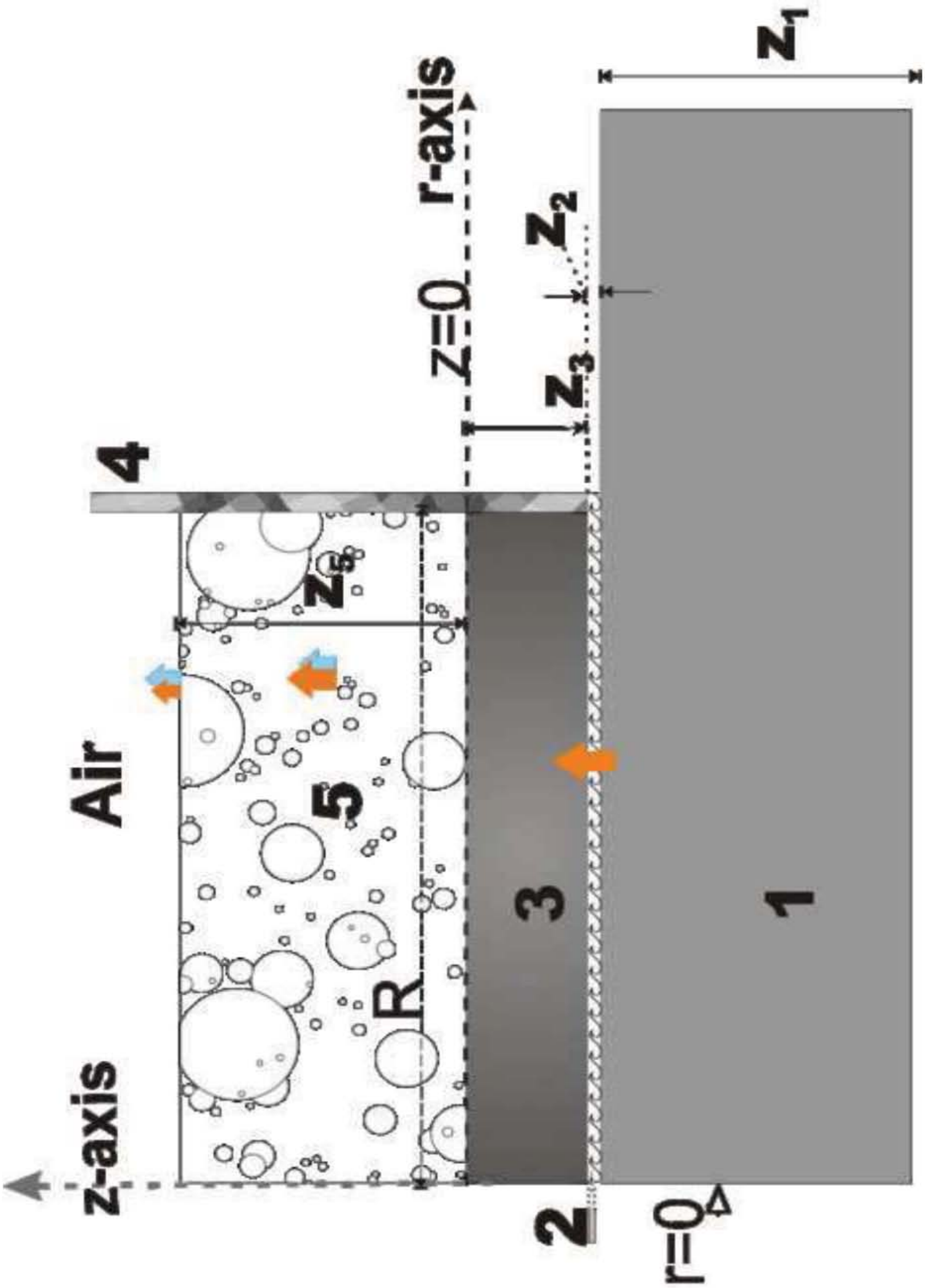

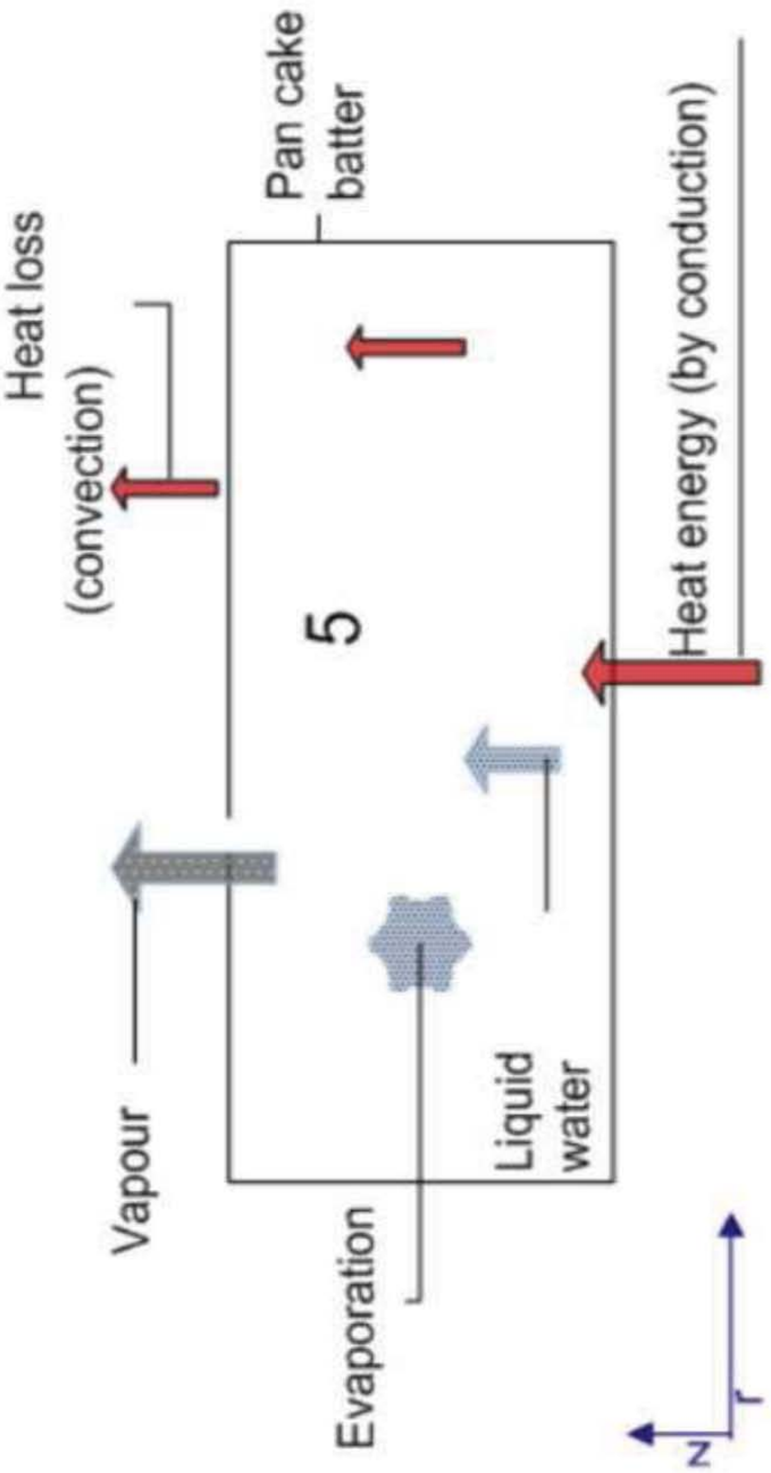

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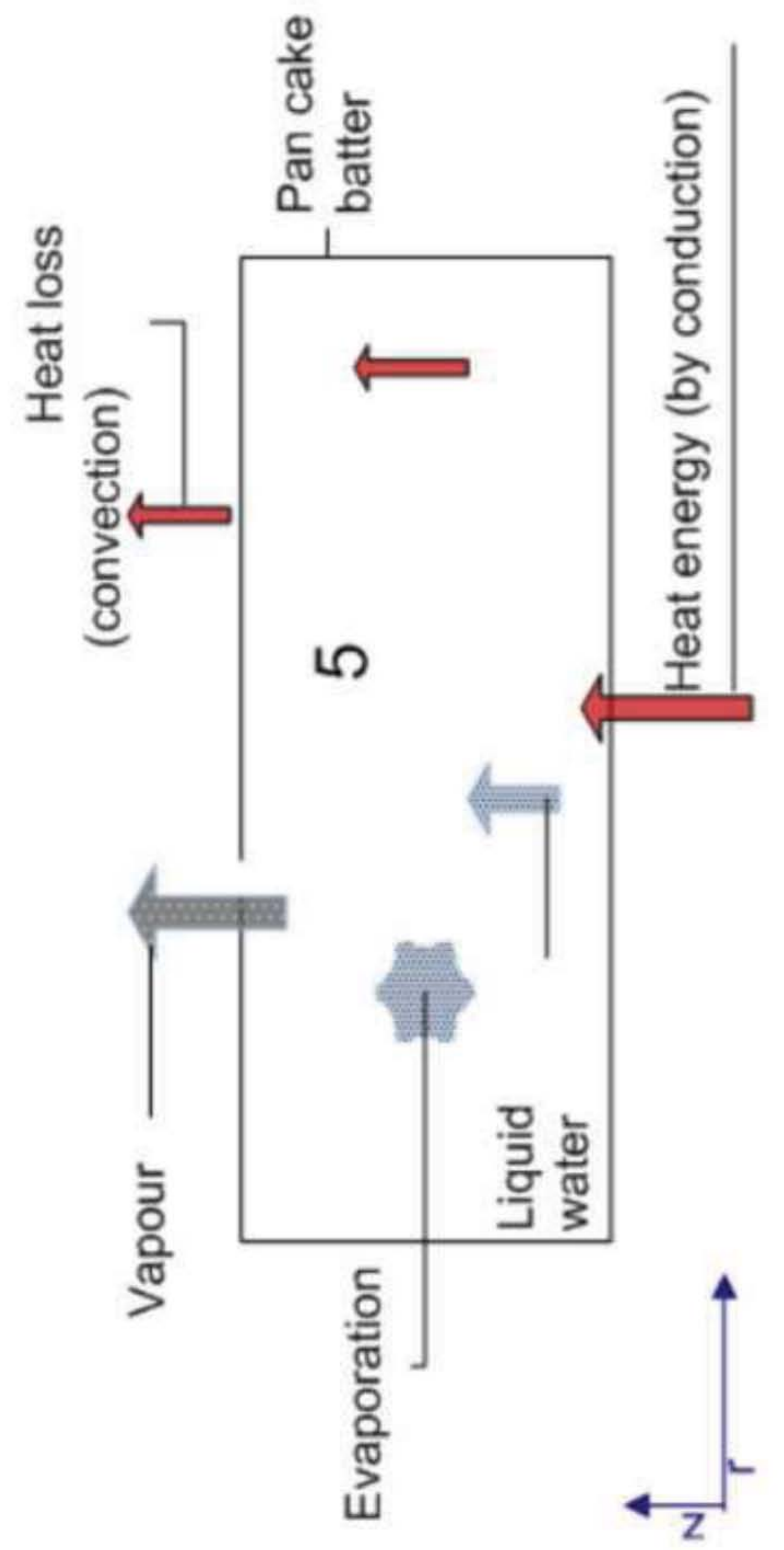

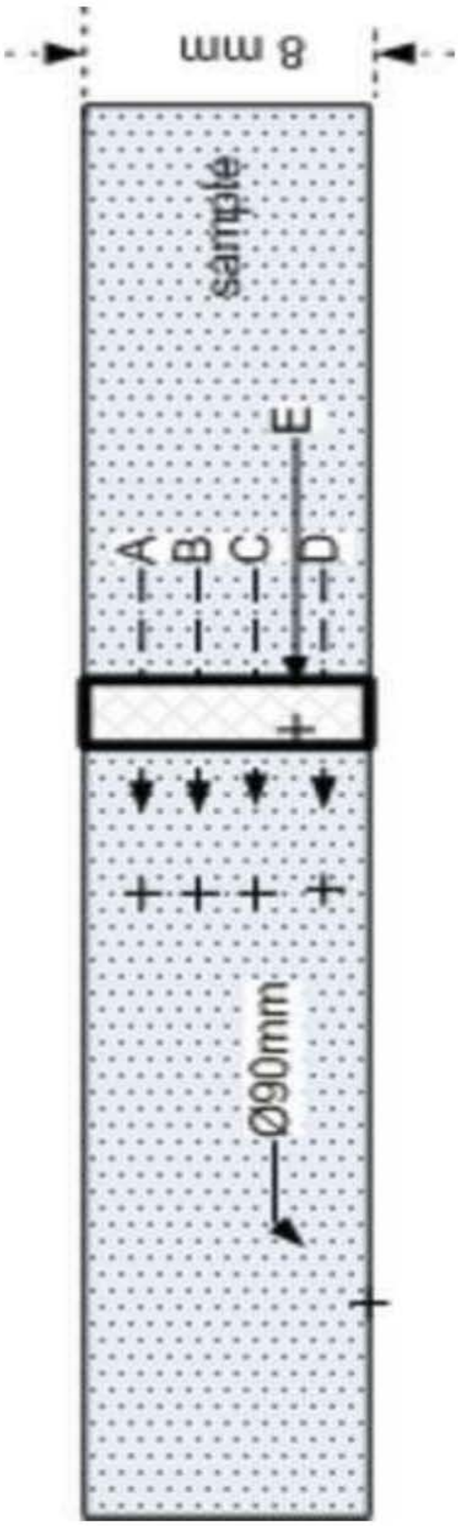

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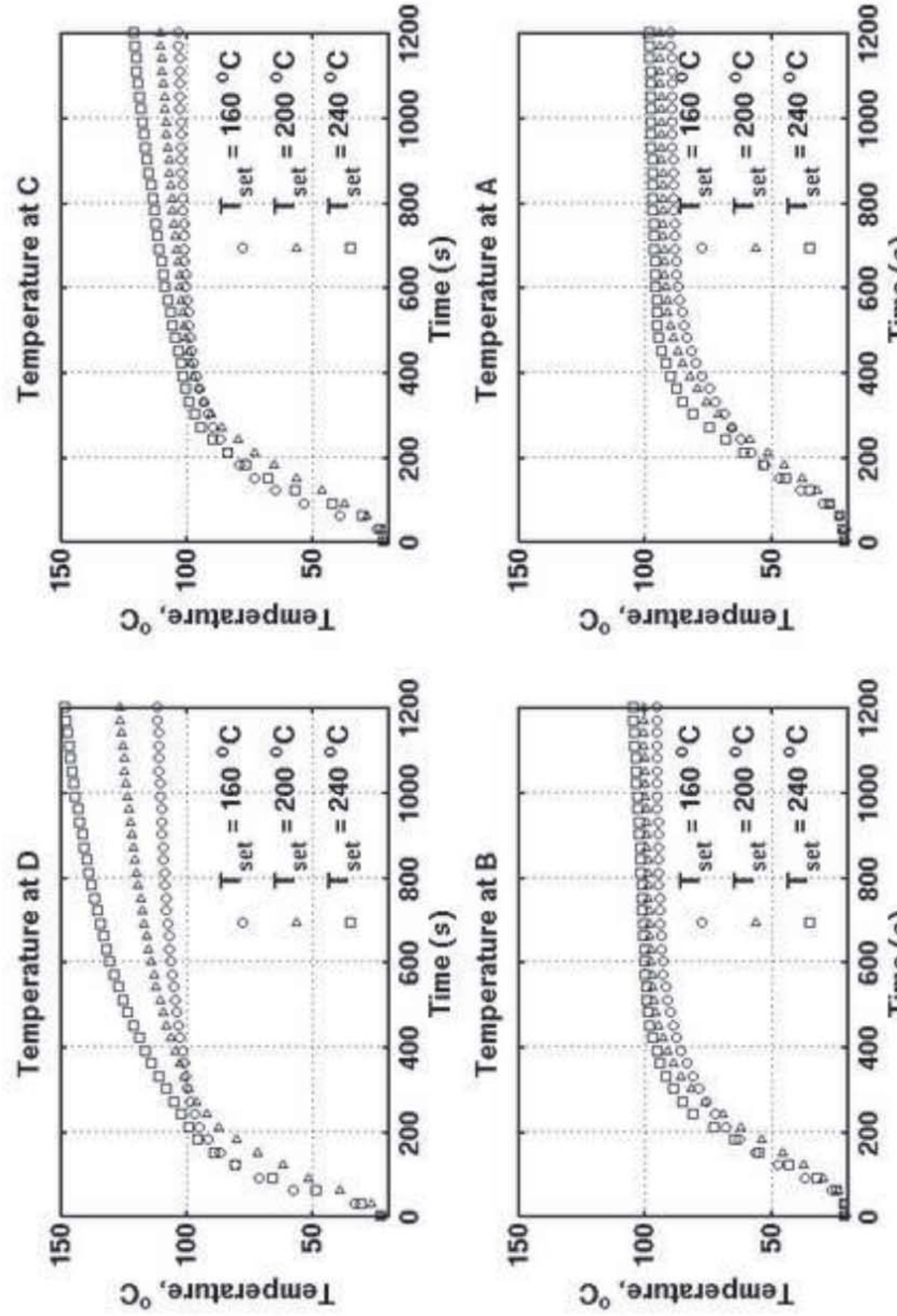

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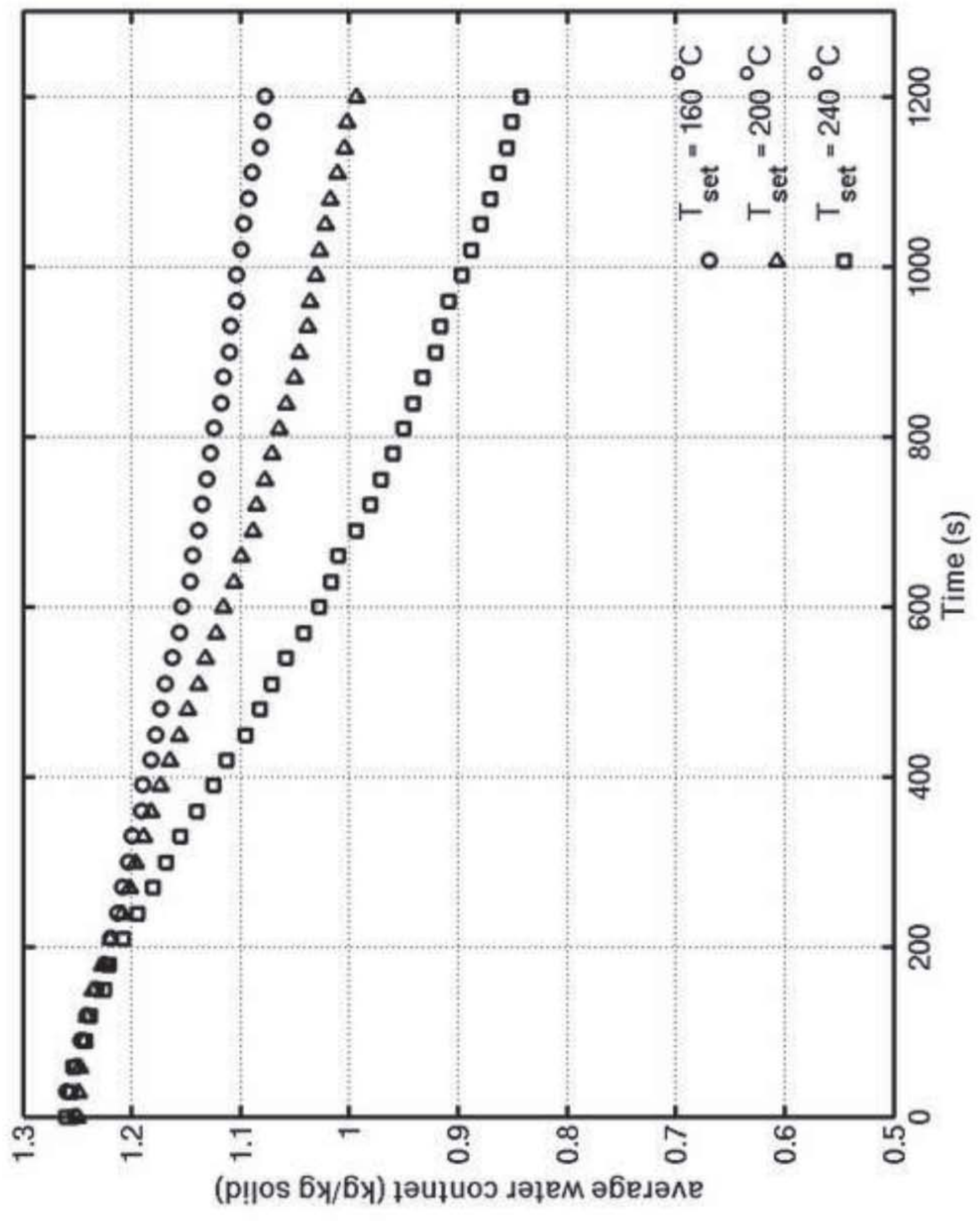

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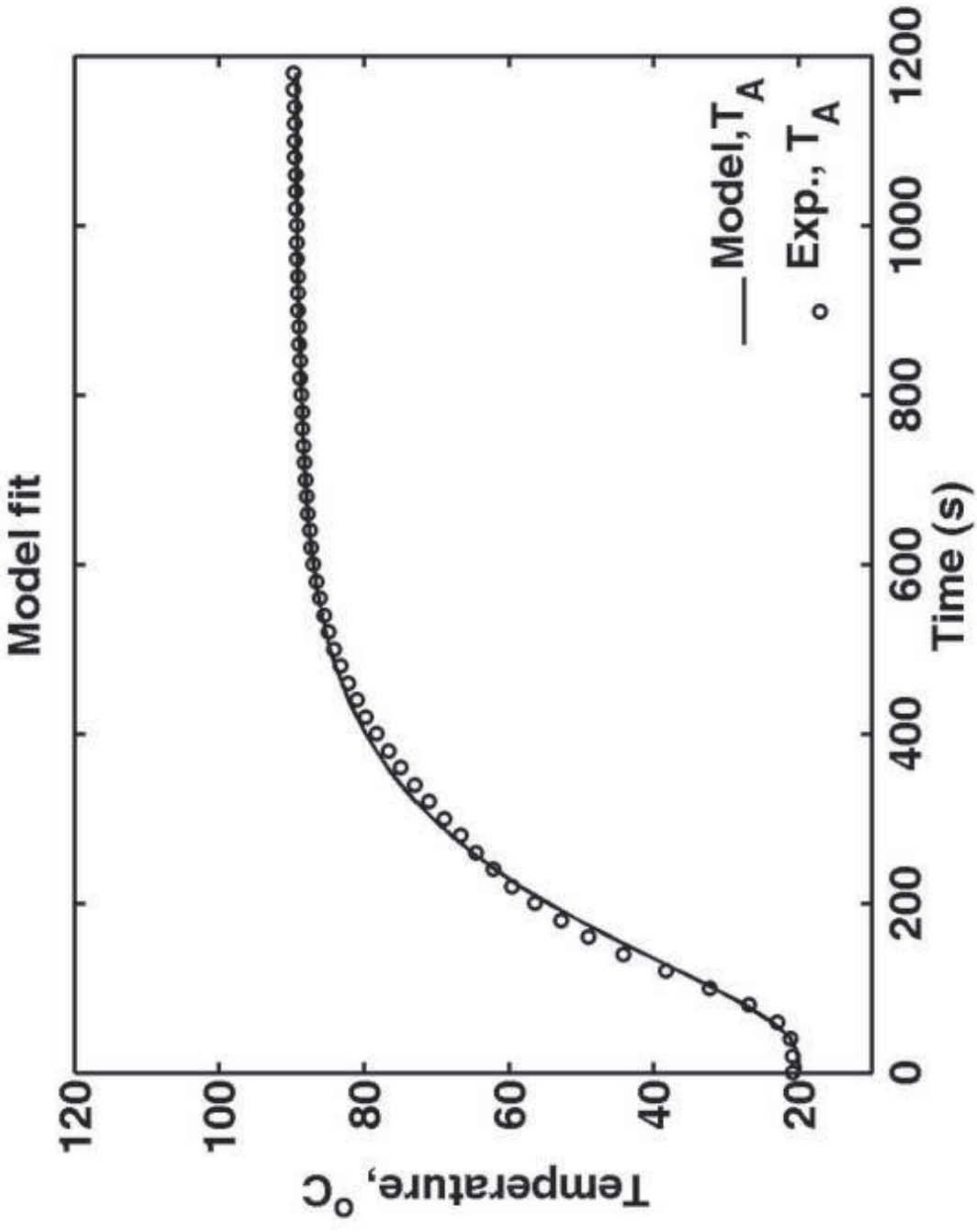

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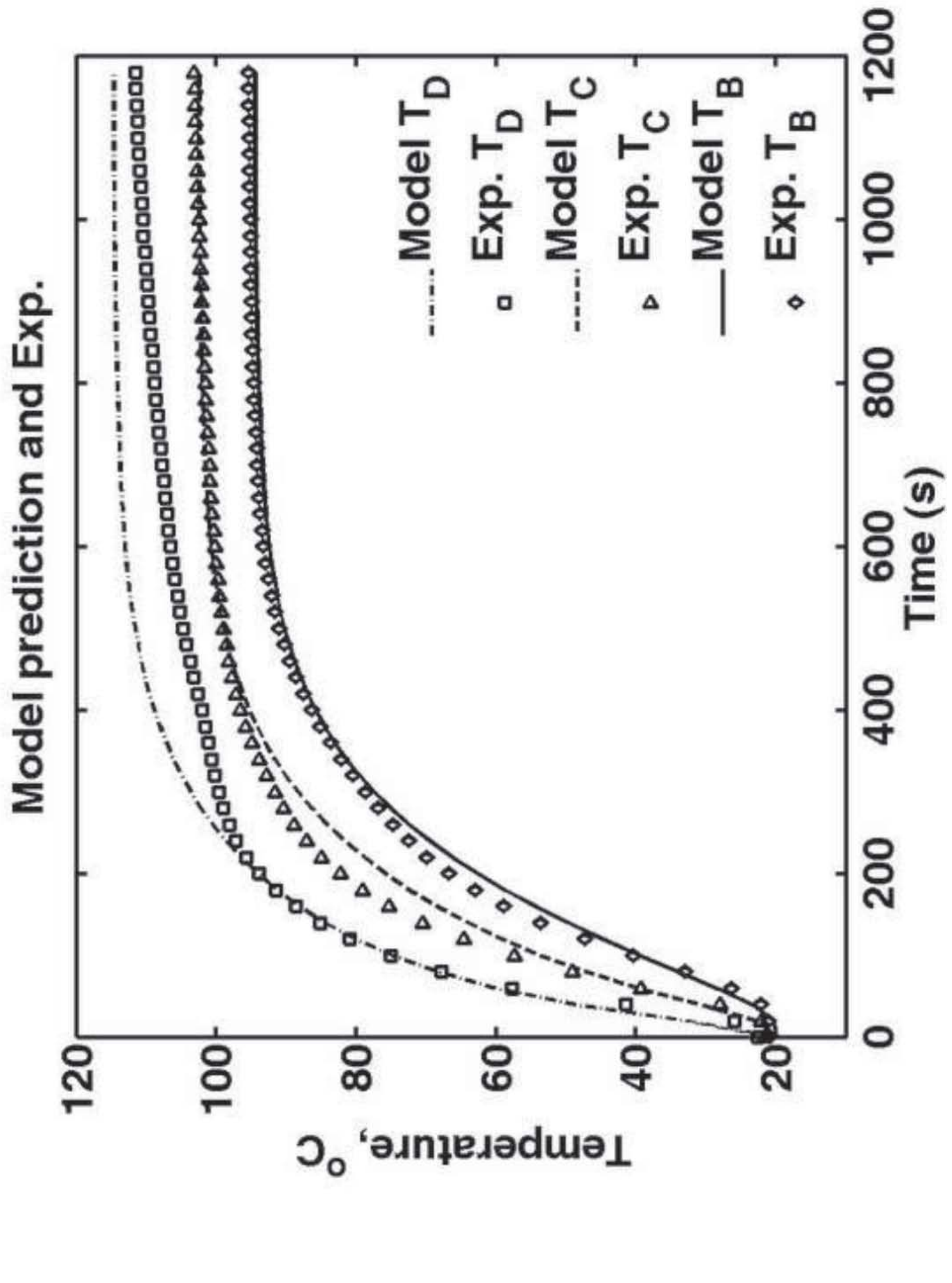

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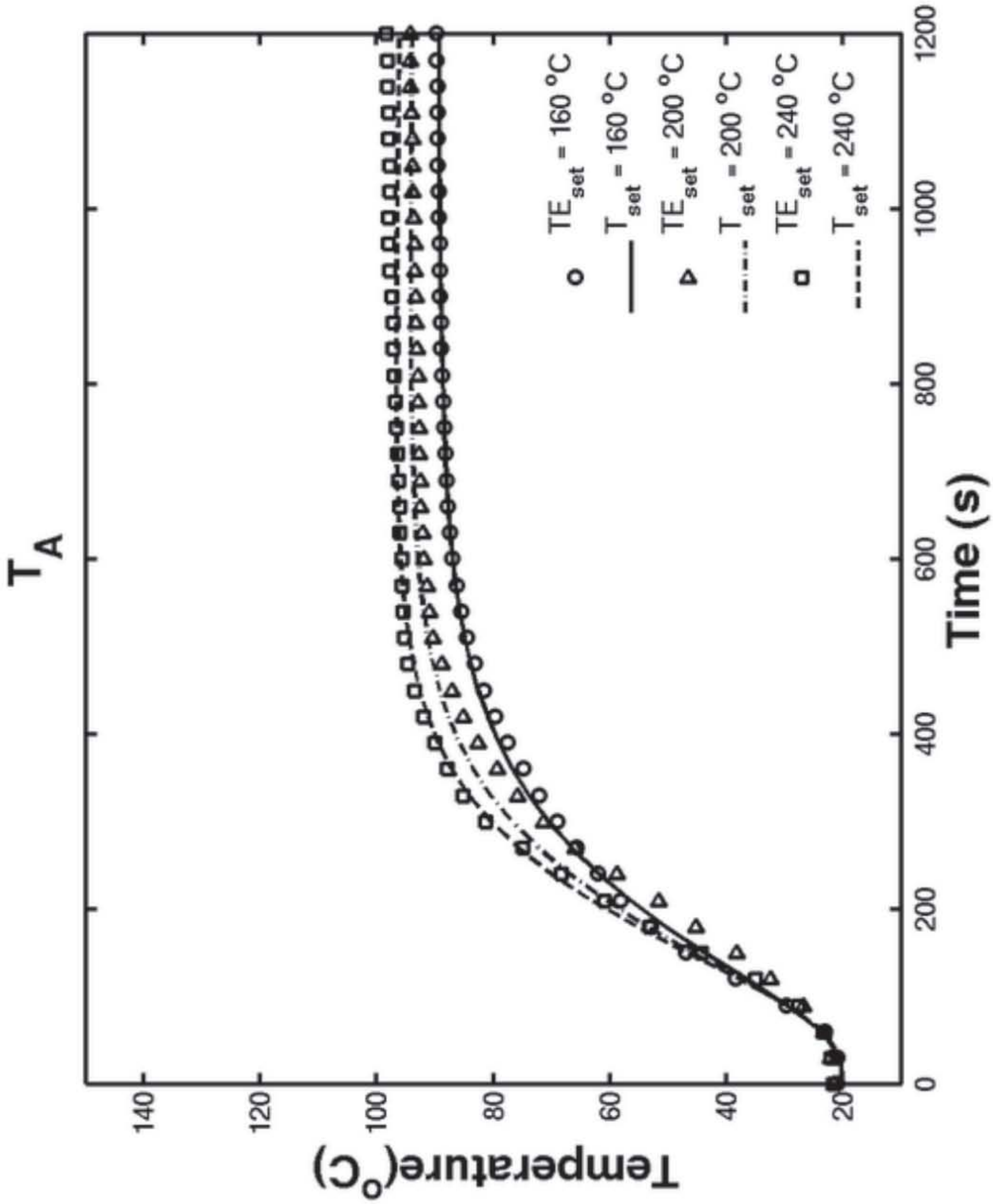

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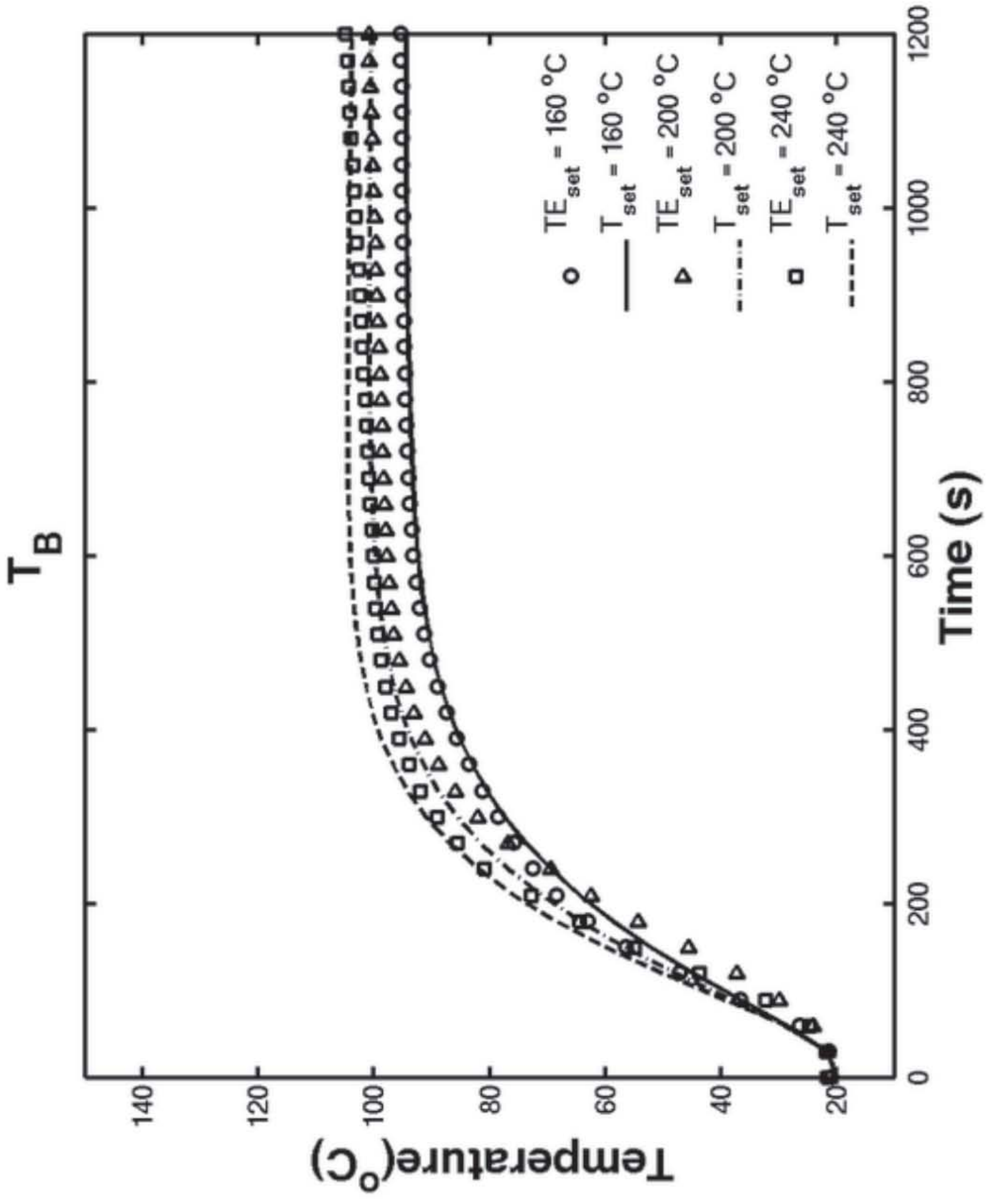

Figure Captions

“Figure caption”

Figure 1 (a): Part of the heating rig used for studying the contact baking process; domain 1 is the rig (aluminum block), domain 2 is the thermal conducting paste (copper paste), domain 3 is the aluminum plate (bottom part of the baking disc), domain 4 is the wall of the baking disc (stainless steel), and domain 5 is the product (pancake batter); (b) Schematic representation of the main phenomena during the contact baking process (within pancake batter)

Figure 2 Temperature sensor position within dough (A = 6.4 mm, B = 4.8 mm, C = 3.2 mm, and D = 1.6 mm from bottom surface, E = the sensor holder)

Figure 3 Temperature profile at different positions (position A, B, C and D) with temperature set point of 160 ^{o}C, 200 ^{o}C, and 240 ^{o}C. The data are only shown with a sampling interval of 30 seconds, for clarity.

Figure 4 Average water content (kg of water / kg of solid) during baking of the pancake batter at three different temperature set points (160 ^{o}C, 200 ^{o}C, and 240 ^{o}C, respectively). The data are only shown with a sampling interval of 30 seconds, for clarity.

Figure 5 Model fit: comparison between measured (o) and simulated (-) temperature profile at position A (T_{set} = 160 ^{O}C).

Figure 6 Model validation: Simulated and measured temperature profiles compared at different positions (B, C and D) for a temperature set point of 160 ^{O}C.

Figure 7 Comparison of simulated and measured temperature profiles at position A with different temperature set point (160 ^{o}C, 200 ^{o}C, and 240 ^{o}C). The data are only shown with a sampling interval of 30 seconds, for clarity.

Figure 8 Comparison of simulated and measured temperature profiles at position B with different temperature set point (160 ^{o}C, 200 ^{o}C, and 240 ^{o}C). The data are only shown with a sampling interval of 30 seconds, for clarity.

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January 2010

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Title of the article:	Modelling of Coupled Heat and Mass Transfer during a Contact Baking Process		
Author(s):	Aberham Hailu Feyissa, Krist Gernaey, Saranya Ashokkumar, Jens Adler-Nissen		
Journal:	Journal of Food Engineering		
PhD-student:	Saranya Ashokkumar	CPR-no.:	201185-3326
Signature of the PhD-student:		Date:	7 December 2010
Co-author:	Aberham Hailu Feyissa	Signature:	
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Description of each author's contribution to the above-mentioned article:

Aberham Hailu Feyissa, as a first author, carried out the modelling work and have written the full manuscript. Saranya Ashokkumar, as a co-author helped to monitor the experimental work. Krist Gernaey and Jens Adler-Nissen, as co-authors reviewed the full manuscript and gave comments and suggestions on the manuscript.

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ISBN: 978-87-92158-89-5